THE BOOK WAS DRENCHED

THE CATALYTIC ACTION

OF SURFACES

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INTRODUCTION.

The friendly reception accorded to the first edition of this book, A Treatise on the Catalytic Action of Surfaces, has stimulated me to prepare a new edition, and, as I have taken advantage of valuable suggestions made by readers, I hope that the presentation of the theory on the catalytic action of surfaces has gained in clearness.

In this book the relation which exists between a variety of processes taking place at catalytically active surfaces is discussed. As the catalytic processes produced by surfaces are of the highest importance to the chemical industry of to-day it would not only have scientific but also practical consequences if a systematization of the existing experience regarding such processes was made possible whereby the chemist could be enabled to foretell the nature of the catalytic surface, the pressure and the temperature able to cause a certain reaction. Such systematization has hitherto been unattainable, and chemists have therefore had to undertake comprehensive research work to obtain information regarding the catalyst wanted, a research which will not necessarily lead to the best possible catalyst. A satisfactory hypothesis able to explain the catalytic action of surfaces has hitherto not been arrived at. The chemist is therefore working blindfold and his selection of a catalyst depends more on a mere chance than on knowledge regarding the qualities of the catalyst wanted.

If one studies the conditions at a metallic surface which has a considerable catalytic effect one is brought to the conclusion that the electronic state of the metal governs the conditions. I therefore looked for conformity between the maximum kinetic energy of the »free« electrons of the metal and the catalytic effect at its surface, and a provisional theory was arrived at.[1,2] A theory indicating the relation which exists between a variety of processes. In this book I

have tried to accurately express the theory which concerns especially the catalytic action of and the adsorption produced at the metallic surfaces. This book will hence be limited to the catalytic action and the adsorption caused by surfaces and the, to a certain degree, related electronic bombardment-reactions although the theory may be applied on the photo effect, the evaporation of ions and electrons from heated surfaces,[2] the enzymic action[3] and the cancer-producing substances.[4]

The assumptions on which the theory is based are included in the following postulates.

Postulate A.

In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperatures in question able to ionize those molecules among the reactants most difficult to ionize and the surface will cause a strong adsorption as ions formed are attracted by the surface.

Postulate B.

A surface able to ionize molecules of a gas or liquid and hence able to yield a strong adsorption produces an increased adsorption when the molecules are substituted by others having a lower ionization potential, assuming that all other conditions are the same.

The highest ionization potential of molecules which can be brought to react catalytically on an active surface or adsorbed strongly should thus indicate *the maximum ability of the surface to cause ionization.* By the use of examples on adsorption and catalysis such ability can be estimated and *a catalytic succession of surfaces* set up. It will further be shown that *the succession is not in contradiction to that ability to cause ionization which a metallic surface has* in accordance with the modern theories on metallic conduction.

The systematisation thereby arrived at is confirmed by its application on several catalytic processes. It might hence enable the chemist to prescribe the most effective catalyst for a given purpose where a surface is able to aid the reaction.

Copenhagen, March 1937.   *J. E. Nyrop.*

CHAPTER I.

CATALYTIC PROCESSES.

A catalytic surface is able to aid a chemical reaction by lowering the energy of activation. Such lowering being produced during adsorption of the reacting molecules by the surface. It is generally understood that a catalyst is a product which furthers a chemical reaction without itself entering *permanently* into the reaction, and which therefore does not occur in the resulting compounds. The usual catalytic designation hence presupposes the formation of intermediate compounds. When caesium, for instance, is adsorbed on nickel, it is known that the adsorbed atom gives up an electron to the nickel and cohesion is produced. Such cohesion is similar in character to that produced when an electron is transfered from one atom to another whereby ionic cohesion is produced. The adsorbed atom is, however, not held to a special atom (ion) of the surface but is free to move along the surface, a true chemical compound is hence not formed although in the limit when the surface is saturated the ratio between the adsorbed atoms and the atoms of the surface may be just as in a chemical compound. A surface of nickel saturated with hydrogen, for intance, is thus able to form a »compound« similar to an unstable hydride NiH_2, and, if the »compounds« formed by adsorption are classed among the intermediate compounds, the usual catalytic designation will cover the catalytic reactions caused by adsorption.

The direct synthetic ammonia process elucidates catalysis generally, it will thus be mentioned in particular as a general example.

Ammonia dissociates into hydrogen and nitrogen at elevated temperatures. At 77°K ammonia is dissociated when conducted through iron pipes but as much as 1050°K is necessary when the dissociation takes place in contact with heated glass. *The surface of iron has therefore a certain catalytic effect exceeding that of glass.* Thermally the formation of one gram mole of ammonia is accompanied by the evolution of 11,780 calories. The percentage of ammonia at equilibrium is therefore greatest at lower temperatures. At 30 atmospheres pressure Haber showed that the percentage of ammonia in a mixture of three parts of hydrogen and 1 part of nitrogen is

°K	% Ammonia
973	0.654
1074	0.344
1174	0.207
1274	0.150

and it was calculated that the amount formed at atmospheric pressure and a temperature of 600°K would be 1.67 % and at 300°K 96 %. At other pressures the yield should be

°K	1 Atm.	100 Atm.	200 Atm.
773	0.130 %	10.7 %	18.1 %
873	0.048 %	4.5 %	8.3 %
973	0.021 %	2.1 %	4.1 %

The highest yield is therefore obtained by the lowest possible temperature but, unfortunately, at temperatures below 750°K the velocity of reaction is too small for commercially practicable operation. The presence of a catalyst increasing the velocity is thus necessary. Haber and co-workers demonstrated that *the reaction is especially furthered by surfaces of Os, Ni, Fe, Mo and W.*

In the Haber process the catalyst used was iron to which a small percentage of alumina was added. The temperature used in the process was 850°K to 1000° and the pressure 200 atmospheres. The Claude process employs 1000 atmospheres and a temperature of 850°K. Claude thereby obtained a concentration of 25 per cent of ammonia and 6 grams of ammonia per hour for each

gram catalyst where Haber only got 6 per cent and half a gram of ammonia. Casale is using 600 atmospheres and 750°K to 850°K the yield of ammonia being 15 per cent, whereas the process of Fauser produces 4 per cent at at pressure af 250 atmospheres and a temperature of 800°K to 850°. The Mont-Cenis process employs a pressure of 100 atmospheres and a temperature of 800°K only. All the methods are modifications of the Haber method and the difference between them is often only of a mechanical nature. The reason for the use of the various pressures is mainly one of economic consideration as high pressures mean small apparatuses, a high yield of ammonia but a large power consumption whereas low pressures mean large apparatuses, low yield but a relatively small power consumption.

The yield of ammonia is a function of the volume of hydrogen-nitrogen mixture passing unit volume of catalyst space per hour. This velocity is termed the *space velocity*. If the flow of gas per hour for every cubic feet of catalyst is 10,000 cubic feet (at normal temperature and pressure) the space velocity is 10,000. When 25 per cent of ammonia is obtained at such velocity, and 10 per cent only if the velocity is increased to 100,000 (pressure and temperature conditions being equal) the yield of ammonia is in the first case 2,500 cubic feet and in the second 10,000. It is therefore quite possible that it pays to use a space velocity yielding only a fraction of the percentage of ammonia indicated by the equilibrium. Enlarged pressure allows an increased space velocity. At 300 atmospheres, for instance, 25 per cent is obtained at a velocity of 10,000 but at 600 atmospheres the velocity can be increased to 50,000 without altering the percentage. The yield of ammonia is in the first case 2,500 cubic feet and in the second 12,500 when the temperature is 750°K. *The yield* of ammonia *can therefore be increased when the pressure and the space-velocity are raised* but, as the percentage of ammonia in the resultant gas decreases with an increase in velocity, the economically best velocity is limited by the difficulties in extracting ammonia from a gas with a small percentage. The optimum velocity is also limited by the power consum-

ed by the transport of the gas and the difficulty of heat exchange between the circulating gases.

The space-velocity does not indicate the velocity with which the gas comes into contact with the catalyst as part of the gas never comes close to the surface of the catalyst as this is covered by that adsorbed layer of hydrogen, nitrogen and ammonia in which the catalytic reaction takes place. The molecules of the passing gas will therefore have to pass through the layer before coming into contact with the surface. The velocity of such passage increases with the partial pressure of the gas in question. Large nitrogen and hydrogen pressure and low pressure of ammonia are therefore necessary as a passage of hydrogen and nitrogen to and ammonia from the catalyst is wanted. A great space-velocity secures such partial pressures and thereby the increased yield of ammonia mentioned.

At low temperatures the equilibrium is favourable to the formation of ammonia but the reaction velocity is slow. At high temperatures, however, the velocity is advantageous but the equilibrium unfavourable. An intermediate optimum temperature will thus exist.

The catalyst used industrially is to-day of the iron type. Pure iron has a great activity but, unfortunately, its activity decreases during the operation. To counteract such decrease small amounts of alumina and potassium are added as *promoters,* and the efficiency of the catalyst is practically speaking made permanent. (It is known that a promoted iron catalyst has retained its high activity for periods of more than a year of work.) Applebey[5] explains the protective effect of the added promoters as due to an altered structure of the catalyst preventing the catalyst from sintering at high temperatures, viz: *the promoter protects the surface of the catalyst.* Wyckoff and Crittenden showed by X-ray studies that *the promoted iron catalyst prepared by reduction after addition of alumina and potassium to the oxide has a smaller crystal unit than pure iron* and that such promoted catalyst showed no signs of grain growth on heating to 920°K. It was, furthermore, indicated that alumina and

potassium oxide exist between the iron crystals. As the pressure is raised a catalyst to which alumina or potassium oxide only has been added decreases in efficiency rapidly, whereas a catalyst promoted with alumina and potassium oxide, a doubly promoted catalyst, retains its efficiency better at high pressure. When the pressure is increased the evolution of heat per unit area of catalyst surface increases. The doubly promoted catalyst is hence more resistant to sintering than the single promoted. That potassium oxides dissociates at a much lower temperature than does potassium aluminate may account for the decreased resistancy of the single promoted catalyst.

Hinshelwood[6] states that *the catalyst reduces the energy of activation.* The energy of activation in question is the apparent energy a lowering of which may represent (1) that energy set free when an activated molecule reacts is used in a more efficient manner for the activation of further molecules when a catalyst is present than when it is absent or (2) that the true energy of activation is reduced. It should also be mentioned that *it is especially the molecules of nitrogen which have to be activated in the synthetic ammonia process.* Emmett and Brunauer, for instance, regard the slow adsorption of nitrogen by various catalysts as being the controlling step in the synthesis.

It has been suggested that the iron catalyst possesses surface atoms that are especially reactive and thus able to form a surface nitride with nitrogen. When this nitride is reduced ammonia should be formed. If the reacting gases contain water vapour, oxygen or carbon monoxide, for instance, the catalytic activity is decreased, viz. the presence of the added gases, even as traces, poison the synthesis. *This poisonous effect is most pronounced at lower temperatures.*

The poisons act by forming an obstructive layer on the surface hindering the free passage of the reacting molecules to the surface or by combining with the especially reactive atoms of the surface and thus hindering the effect.

If carbon monoxide and hydrogen react in the presence of nickel methane, carbon dioxide and water are produced, if an oxide

catalyst is employed at high pressure methanol is formed. Copper produces mainly formaldehyde. *A variation in the catalyst hence produce a change of the ultimate products.*

Burk[7] describes some of the ways in which bonds in an adsorbed molecule can be loosened and the energy of activation thus lowered. *The Atomic Distortion Theory and the Molecular Distortion Theory* are mentioned in this connection. By the first theory is assumed that molecules adsorbed on a surface are held on the surface by ordinary valence forces whereby a rearrangement of the electrons of the atoms constituting the molecules takes place. The chemical properties are thus altered and the adsorbed molecules should become more reactive. By the other theory it is suggested that adsorptive forces lower the energy of activation by separating the atoms forming the bond which is to be broken. Burk seems to be against the Atomic Distortion Theory as the energy necessary to dissociate an excited molecule is sometimes about the same as that for the unexcited one, and also the rate of decomposition of nitrogen pentoxide is about the same in the gas phase as in a solution of chloroform which must have a large electric momentum. Burk shows in favour of the Molecular Distortion Theory that the atoms forming the bond which is to be broken could be separated in case the molecules containing the atoms were adsorbed at more than one point. Taylor suggests that molecules are dissociated close to an active surface. Burk is against such assumption as molecules with loosened bonds should be more reactive than atoms kept to the surface by valency forces. A catalyst could also be able to ionize the adsorbed gases but Burk is also against such supposition as some experiments of Hinchelwood show that the relative difficulty of decomposing ammonia and nitrous oxide by molecular collision is maintained when the molecules to be decomposed collides with ions. Burk seems in this case to forget that decomposing by molecular collision is furthered when the reacting molecules themselves are ionized and not alone certain molecules with which the reacting molecules collide. On the other hand Burk states that »there is considerable evidence of electrical effects accompanying adsorption in some cases.«

When in the following *the active surface of a catalyst* is mentioned this will not mean the apparent surface but only *the area accessible to the reacting molecules*. The whole of the internal surface of a porous catalyst is for instance not always active, as a condensation in the pores will hinder the necessary free passage to and from the surface. Bowden and O'Connor[8] have demonstrated that the accessible area of a solidified alloy is 1.4, when that of the molten alloy is 1.0. If such surface is scratched with sand-paper the surface is increased to 6.3, and it is enlarged to 800 by etching. Many catalysts have even a relatively larger surface.

Every surface has as a rule a certain catalytic effect, as the presence of a surface often increases the velocity of reaction, but only surfaces of metals, certain oxides, sulphides, carbides, and a few other substances have sufficiently great catalytic effect to be of practical importance. The feeble action of many surfaces is due to a Van der Waals' adsorption causing an increased concentration of molecules close to the surface, the number of collisions between the molecules is thus increased whereby the velocity of reaction is enlarged. In this way it is, however, quite impossible to explain the strong catalytic effect and the adsorption caused by the above mentioned products.

In the opinion of several investigators a formation of intermediate compounds should always explain catalysis. Sabatier and Senderens in considering the hydrogenation processes taking place on nickel suggest that an *unstable* hydride NiH_2 is produced and Frankenburger in considering the decomposition of ammonia on tungsten assumes that hydrogen is set free as compounds like $W_X NH$ or $W_X N_2$ are formed. In these cases a saturated ionic adsorption is however quite possible and the intermediate compound is then equal to an adsorption complex.

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The theory, which will be expounded in this book, is based upon the assumption that *the electronic state of a catalyst is able to cause ionization of certain molecules brought close to the catalytic surface*. The assumptions on which the theory is based can be given the following form.

Postulate A.

In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperatures in question able to ionize those molecules among the reactants most difficult to ionize, and the surface will cause a strong adsorption as ions formed are attracted by the surface.

Postulate B.

A surface able to ionize molecules of a gas or liquid, and hence able to yield a strong adsorption, produces an increased adsorption when the molecules are substituted by others having a lower ionization potential, assuming that all other conditions are the same.

When the intermediate complex theory is maintained the adsorbed molecule (or atom) becomes by ionization the positive partner in a combination of the surface and the molecule (atom).

If molecules come close to a catalytic surface able to produce ionization, that dissociation, for instance, which can be produced when molecules collide, is favoured, as the activation energy necessary in dissociating ions is generally less than the energy required by the corresponding neutral molecules. When a hydrogen molecule is dissociated two nuclei kept together by two electrons will be separated, whereas in dissociation of a hydrogen ion one electron only keeps the nuclei together. It thus takes more energy to dissociate a hydrogen molecule than an ion and *part of the energy used for ionization therefore reappears as a decrease in the energy of dissociation.* Hydrogen molecules demand an energy equal to 4.4 electron-volts when dissociation shall occur but hydrogen ions require 2.6 volts only. For molecules of nitrogen and oxygen energies of 11.4 and 7.1 volts (in the following »volts« shall often be used instead of »electron-volts«) are necessary in case dissociation shall take place but the ionized molecules only require 9.1 and 6.5 volts respectively.

In the following chapters it will be explained how the adsorption caused by ionization influences the catalytic processes and it will also be demonstrated that *only catalysts having certain qualities,*

characterised by their electronic state, are able to aid a given process.

The new theory of catalysis was initiated by the experience gained regarding electronic bombardment-synthesis in gas mixtures which occurs only when the accelerating voltage is higher than the ionization potential of those molecules amongst the reactants most difficult to ionize. A condition similar to Postulate A.

CHAPTER II.

ADSORPTION AND SOLUTION.

It is generally accepted that at least two kinds of adsorption exist, i. e. a *weak adsorption* predominant at lower temperatures and a *strong adsorption* that for every gas is caused by certain surfaces only and above a certain temperature. The weak adsorption, called physical or van der Waals' adsorption, being due to the field of force surrounding the neutral atom or molecule, the strong adsorption, sometimes called chemisorption or activated adsorption, being due to forces similar in nature to those of chemical combination. It is this strong adsorption that should be due to ionization.

If an active surface is placed in a gas having an energy of ionization q and the surface is, in accordance to *Postulate A*, able to ionize molecules with an energy of ionization Q or less,

$$(1) \qquad \begin{aligned} S &= e^{A(Q \,\div\, q)} & (Q \geqq q) \\ S &= 0 & (Q < q) \end{aligned}$$

will represent the *ability of the surface to ionize the gas molecules in question and Q the »Ability of the surface to cause Ionization«.* (Q may vary with temperature, see Chapter VII). An increase in molecular concentration at the surface is produced when the ionization causes a time lag between the arrival and evaporation of molecules colliding with the surface. If it is assumed that after an average time $\triangle t$ has elapsed an ion at the surface will be neutralized and, the molecule formed will, after the expiration of an

average time varying as S^{-1}, again have the possibility of being ionized the adsorption can be calculated.

Neutralization of ions at the surface occurs if electrons are present at the surface. When it is assumed that electrons are present and the surface has at the same time ability to cause ionization, the *ionization* becomes *intermittent*.

The number of molecular collisions per sq. cm of surface per second in which the component of velocity perpendicular to the surface is so small, that a molecule entering the zone at the surface wherein ionization occurs has the possibility of being ionized is

$$(2) \qquad N_1 = c_1 \, n \, \sqrt{\frac{2kT}{\pi m}} \left(1 - e^{-m \left(\frac{d}{c}\right)^2 S^2/2kT}\right),$$

where n is the number of molecules per cc apart from the surface, m the weight of a molecule, k the molecular gas constant, T the temperature and d the width of the zone. c and c_1 being constants.

The time during which the molecules, retarded in their movements away from the surface by the ionization, are in their neutral state is $\dfrac{cS^{-1}}{\triangle t + cS^{-1}}$ of the whole time the molecules are delayed in the zone. If during such time a molecule shall be expelled from the surface it will have to collide with another molecule having such velocity and direction that the adsorbed molecule is brought outside the zone before it has the possibility of again being ionized. The number of collisions per sq. cm per second in which the component of velocity perpendicular to the surface is large enough to cause the expelling is

$$\frac{n}{2} \sqrt{\frac{2kT}{\pi m}} \; e^{-m \left(\frac{d}{c}\right)^2 S^2/2kT}$$

Considering also collisions among the adsorbed molecules, the number of molecules expelled from one sq. cm. per second is

$$(3) \quad N_2 = c_2 \, (n + a n_1) \, r^2 \sqrt{\frac{3kT}{m}} \; n_1 \, d \, \frac{cS^{-1}}{\triangle t + cS^{-1}} \sqrt{\frac{2kT}{\pi m}} \; e^{-m \left(\frac{d}{c}\right)^2 S^2/2kT}$$

where c_2 and a are constants (a $<$ 1), r the radius of the molecules and n_1 the number of molecules adsorbed per cc of the zone.

At equilibrium $N_1 = N_2$ and the adsorption becomes

$$n_1 = \frac{n (\wedge t + cS^{-1})}{c' S^{-1} (n + an_1) r^2 d} \left(\frac{m}{kT}\right)^{1/2} (e^{m \left(\frac{d}{c}\right)^2 S^2/2kT} - 1).$$

As $\dfrac{1}{d}$ is the surface on which n_1 molecules are adsorbed, the

volume of gas adsorbed on a surface A becomes

$$(4) \qquad R = \frac{k_0 An (1 + k_1 S)}{r^2 (n + an_1)} \left(\frac{m}{kT}\right)^{1/2} (e^{m \left(\frac{d}{c}\right)^2 S^2/2kT} - 1),$$

where k_0 and k_1 are constants.

At such high temperatures where ionic emission is appreciable, the adsorption becomes less as not molecules or atoms alone but also ions will evaporate.

When an_1 is small compared with n, i. e. *at high pressures,* we have approximately

$$(5) \qquad R_p = \frac{k_0 A (1 + k_1 S)}{r^2} \left(\frac{m}{kT}\right)^{1/2} e^{m \left(\frac{d}{c}\right)^2 S^2/2kT}.$$

At those high pressures where (5) can be used the adsorption is uninfluenced of the pressure. That there is such a maximum of adsorption in existence — *a saturation pressure* — is confirmed by experiments.

As to the saturation pressure Gauger and Taylor[9] have shown that a surface of nickel is saturated with hydrogen at a pressure of 40 mm when the temperature is 298°K and that a 19-fold increase in pressure does not add to the adsorption which on a certain amount of nickel is 8.7 cc. At 578°K the saturation pressure is 250 mm and the adsorbed volume 5.5 cc. The adsorption of hydrogen, carbon monoxide and carbon dioxide on copper show similar adsorption maxima. Dew has shown that the adsorption of hydrogen on copper at 273°K and 383°K is as 10 to 8.7 when the adsorption takes place above the saturation pressures.

At very low pressures (4) shows that *the amount adsorbed is proportional to the pressure*. If the above mentioned neutralisation of the ions formed did not take place and the ionization was not intermittent the adsorption would not at low pressures be proportional to the pressure, a proportionality which has been confirmed by experiments.

If a dissociation, $A_2 \longrightarrow 2A$, is produced during the adsorption, the volume of gas adsorbed becomes

$$(6) \quad R = \frac{k_0 \, A \, n \, (1 + k_1 S) \, (1 - e^{-m \left(\frac{d}{c}\right)^2 S^2/2kT}) \, m^{1/2}}{(kT)^{1/2}\left(\left(\frac{r + r_1}{2}\right)^2 n \, e^{-\frac{9}{16} m \left(\frac{d}{c}\right)^2 S^2/kT} + a r_1^2 n_1 e^{-1/2 \, m \left(\frac{d}{c}\right)^2 S^2/kT}\right)},$$

and at high pressures

$$(7) \quad R_p = \frac{k_0 \, A \, (1 + k_1 S)}{\left(\frac{r + r_1}{2}\right)^2} \left(\frac{m}{kT}\right)^{1/2} e^{\frac{9}{16} m \left(\frac{d}{c}\right)^2 S^2/kT},$$

where r_1 is the radius of the adsorbed radical or atom. If the molecular weight is decreased during adsorption, the adsorption will diminish if, at the same time, S^2 is not enlarged correspondingly. If hydrogen, for instance, is adsorbed and, at a certain temperature dissociation sets in, the ionization potential, q, decreases from 15,4 to 13,5 volts. S^2 can thus easily be increased so much that the increase overshadows the effect of the halving of the weight. At such temperature the adsorption will pass through a minimum. Frankenburger and Hodler[26] showed that within 370°K to 450°K and at a definite pressure the amount of hydrogen adsorbed on tungsten increased with increase in temperature in contradiction to the generally accepted inverse dependence.

A catalytic surface of copper adsorbing 8.55 cc ethylene at a pressure of 380 mm and a temperature of 298°K adsorbs 3.25 cc of hydrogen. If the catalyst is heated to 573°K in the presence of mercury the surface adsorbs mercurial vapours. If evacuation and cooling to a temperature of 298°K take place after the treatment

with mercury it can be estimated that the mercury adsorbed is approximately equal to that amount which would be adsorbed from vapours having a pressure of 0.05 mm. The catalyst treated in this manner adsorbs according to experiments of Pease 6.70 cc of ethylene and 0.15 cc of hydrogen. This large decrease in the adsorptive power of copper with regard to hydrogen Adam[10] has attributed to differing capacities of patches to adsorb hydrogen and ethylene respectively, and mercury vapours being preferentially adsorbed on those patches which have hydrogen-adsorbing capacity. Such an assumption is quite superfluous when Postulate B is considered as the theory on the strong adsorption caused by ionization explains the preferential adsorption mentioned, an adsorption often appearing as a poisoning. If mercury is ionized by 10.4 volts, ethylene by 12.3 and, in accordance with Bleakney,[11] hydrogen by 15.37 the ability of the surface to cause ionization will in accordance to Postulate A, be about 15.5—16.5 volts if hydrogen is weakly adsorbed, ethylene strongly and mercury most of all. Pease has further demonstrated that the adsorption of carbon monoxide on the same catalyst is reduced by 50 per cent in the presence of mercury. As carbon monoxide is ionized in the gas phase at about 15 volts this is also in agreement with the theory.

A clean platinum catalyst, for instance, hydrogenates propyl ketone, after poisoning with a small amount of carbon disulphide propyl ketone cannot be hydrogenated but piperonal is still hydrogenated. A further addition of carbon disulphide prevents the reduction of piperonal, but leaves the power of reducing nitrobenzene.[12] This has also lead to the suggestion that a catalytic surface contains active patches, the greater part of the surface being inactive, but, also in this case we may be content with the preferential adsorption that is a consequence of the difference in ionization potential of the molecules adsorbed. (With such complex molecules the dimensions of the molecules in relation to the width of the surface zone may also have to be taken into consideration). *The surface of a homogeneous catalyst should thus be without certain active patches.* A surface of a catalyst may, however, be composed of different crystal surfaces, and as the ability to cause ionization

at such surface may not be the same, the adsorption will vary along the surface. The processes caused by a heterogeneous surface are therefore composed of the reactions above the various crystal surfaces, and of those reactions taking place at the boundary between the crystals, as different adsorption takes place on each side of the boundary. If on one crystal a reaction $A + nB = C$ takes place and above another $A + mB = D$, it is possible that compounds of C and D are produced above the boundary between the crystals.

By the just mentioned poisoning of a copper surface by low pressure mercury vapours, mercury was adsorbed. If the vapour pressure is increased the amount of mercury adsorbed will increase. The specific metallic character of the ions may thereby be enhanced and finally the adsorbed ions may approach so closely to each other that a metallic lattice is produced. The surface is then one of mercury instead of one of copper. This new surface has a quite other adsorptive power than the old one and is unable to a adsorb hydrogen and carbon monoxide, for instance. (As long as the mercury atoms only were present as scattered ions carbon monoxide was adsorbed).

As mercury vapours expel hydrogen from a surface of copper it explains how hydrogenation of carbon monoxide on a surface of copper is prevented by the presence of mercury. When hydrogenation of the monoxide takes place on copper, methane is produced and, as the ionization energy of these products is between 13.7 and 15 volts, none of them take up the space of the surface zone preferentially. If three volumes of hydrogen and one volume of nitrogen pass over a surface of nickel or one of iron at certain temperatures and pressures ammonia is produced, and the best result is obtained when the adsorption takes place in the proportion 3 to 1. In accordance with technical results this takes place on iron. If the energy of ionization for hydrogen is 15.37 volts and for nitrogen 16.7 the ability of the iron surface to cause ionization should be about 18 volts.

That the proportion between the adsorption of carbon monoxide ɳd hydrogen on nickel is 0.87, on platinum 3.3 and on copper 8

is also in agreement with the Postulates A and B when the ability of the surface of platinum to ionize is less than the corresponding ability of nickel but larger than copper.

Hirst and Rideal[13] were able to show that the maximum adsorption for carbon oxide on copper can be 8 times the adsorption of hydrogen. Considering ionic adsorption and an ionization potential of the oxide of 15 volts and of hydrogen 15,37 volts, the ability of copper at the temperature in question should be about 15.5 volts. Maxted[14] demonstrated further that the adsorption of lead ions from a solution on a platinum catalyst was 1.5 times the adsorption of mercury ions. The ionization potential of lead being between 7.4 and 8.3 volts and of mercury 10.4 volts. There is thus agreement with Postulate B, especially as the difference in atomic weight is 3 % only. On copper, cobalt and iron the adsorption of hydrogen at the temperatures in question is less than that of carbon dioxide but on platinum and palladium much larger as a solution of the hydrogen in the metal sets in so that the adsorption will appear to be much larger.

Copper adsorbs more ethylene than carbon monoxide and more of the monoxide than hydrogen when the pressure is above the saturation pressure. This is a direct consequence of the decreasing energy of ionization of the adsorbed molecules. At lower pressures, on the other hand, where the adsorption is a function of the pressure, a succession of carbon monoxide, ethylene and hydrogen has been observed. Considering equation (4) and (6) this may be explicable, as low pressure may further the dissociation of hydrogen.

When nitrogen is adsorbed on iron a van der Waals' adsorption only is measureable up to 270°K where activated adsorption sets in with the result that the total adsorption is greater at temperatures above 270°K than below. For carbon oxide the physical adsorption is predominant below 200°K and an activated adsorption sets in at this temperature.

When gases like *hydrogen and nitrogen* are adsorbed we have seen that they may be expected to be adsorbed as *positive ions.*

When *oxygen and the halogens* are adsorbed adsorption as positive
ions may be possible but the *adsorption as negative ions* will be the
rule. We shall later see that positive ions are more strongly bound
to a metal surface than negative and that in the catalytic reaction
it is the formation of positive ions that are of especial importance.

The kinetic energy of adsorbed ions increases with enhanced
temperature. Some of the ions will thereby acquire energy high
enough to leave the surface zone, viz: *ions are* ejected *from the
surface during evaporation of the adsorbed film.*

The assumed intermittent ionization producing a strong ad-
sorption on metallic surfaces attempts to keep the ions in a zone
close to the surface, a zone which shall be termed the *»positive
zone«*. Ionization, however, does not influence the movements of the
molecules (ions) parallel to the surface. Germer has observed that
X-rays are scattered from an adsorbed layer separated by a definite
distance from the surface. On heating, a layer in a regular distance
disappears although gas is still on the surface. (On heating, the gas
layer only weakens beams scattered by the substratum ions of the
metal). This shows that most of the adsorbed molecules (ions)
move in a zone a certain distance off the surface at ordinary
temperatures, but at raised temperatures the X-rays will not show
a specific distance as the ions will oscillate about the zone.

When equation (4) is considered the *positive ion emission* from
a gas layer adsorbed on a surface having ability to cause ionization
becomes at low pressures

(8) $$J = C_0 \, n \, \triangle t \, S \, e^{\left(\frac{1}{2} \, m \, \left(\frac{d}{c}\right)^2 S^2 \, - \, \frac{W}{\alpha}\right)/kT}$$

where W/α is the work function for the adsorbed positive ion
$(\alpha > 1)$. W is the maximum work function for a positive ion which
is not hindered, either by its »size« nor by previous adsorbed ions,
in approaching that zone near the surface where the work function
is a maximum. As $\frac{1}{2} \, m \, \left(\frac{d}{c}\right)^{2'} S^2$ is small compared with W/α and

as there is reason to believe that $\triangle t$ vary as q^{-1} we have approximately

$$(8^1) \qquad J = C' \, n \, \frac{S}{q} \, e^{-\,W/\alpha kT} \; .$$

J is thus rapidly decreasing when the ionization energy of the adsorbed molecules (or atoms) is enlarged and the ion current that can be drawn will be governed by the vapour density of the gas. As a first approximation α is proportional to the »radii« of the adsorbed moleculer (or atoms). If the work function of cæsium adsorbed on a given surface is W_0, the following table gives the work function, φ, for other ions adsorbed on the same surface.

Ion	φ	Ion	φ
Cs	W_0	Tl	1.63 c W_0
Rb	1.16 c W_0	Cu	1.71 c W_0
K	1.36 c W_0	Na	1.77 c W_0
In	1.56 c W_0	Ga	1.97 c W_0

(Where c is a factor determined by experiments).

Moon and Oliphant[15] showed that the rate of evaporation of positive ions is a liniar function of the surface concentration. They further conclude from experiments with the re-emission of potassium ions that such emission is a process of evaporation rather than instantaneous reflection. Powell and Brata[16] conclude from experiments with a known number of metallic atoms deposited on to an iron oxide surface and the evaporation of the atoms as ions that the work function for indium ions is less than that for thallium, and that gallium has a higher work function. Further, it is known that a higher temperature is required to evaporate monoatomic layers of potassium than of rubidium ions and of rubidium than of cæsium ions, from surfaces of pure tungsten. The measured positive ion work function of tungsten is for potassium ions 2.43 volts, for rubidium 2.14 and for cæsium 1.81 volts. This is all in agreement with the order of magnitude of the table and with equation (8^1). c is thus 1.01. Only part of the ions ejected will move into such distance from the surface that the existence of them can be

proved and, as there exists a probability that a positive ion whose ionization energy is greater than the electronic work function, φ, of the surface can capture an electron even at some distance from the surface, the positive ion emission is suppressed when $q > \varphi$.

Morozov[17] showed that when hydrogen is adsorbed on iron three adsorption processes exist, viz. low temperature van der Waals' adsorption, activated adsorption and activated diffusion. Considering activated adsorption caused by ionization work, W/α, will have to be performed when an ion is emitted. In the same manner a potential barrier will have to be surmounted if the ion shall pass from just outside of the surface to the interior of a metal. When this barrier has been passed the ion may diffuse freely in the metal. Coehn and Specht[18] found that the diffusion of hydrogen in palladium is normal and that in case a potential is applied to a palladium wire loaded with hydrogen the rate of diffusion of hydrogen to the negative end of the wire is increased. Franzini[19] showed furthermore that hydrogen is rapidly removed from a hydrogenated palladium wire when applying a negative potential to a cylindrical plate surrounding the wire. This demonstrates that the hydrogen is present in the metal as ions. Also in nickel and iron Franzini was able to show that hydrogen was at least partially present as positive ions. Coehn and Sperling[20] was further able to demonstrate that platinum, iron and nickel absorb 0.01, 0.2 and 0.7 mg hydrogen per 100 g metal at $1100^\circ K$. An absorption of the same order of magnitude as the adsorption at this high temperature on the surface of the respective metals. Ward[21] shows that in all likelihood the rate of solution of hydrogen into copper is proportional to the amount of gas adsorbed on the surface. Benton[22] demonstrated that the solubility does not make its appearance until temperatures are reached at which there is a pronounced activated adsorption. This fact suggests, as pointed out by Benton, *that activated adsorption is a necessary precedent to solution.* Considering ionic adsorption of diatomic molecules, the molecules are intermittently ionized when the temperature is above a certain minimum temperature. As the ionized molecules have a decreased energy of dissociation, atoms will be formed and the relative num-

ber of dissociated molecules will increase when the temperature is raised. At the surface the atoms are also ionized intermittently and, as mentioned above, hydrogen is present as ions in certain metals. The question is thus (i) are ions, formed at the surface, surmounting the potential barrier mentioned in passing from just outside the surface to the interior of the metal, or (ii) are atoms, present at the surface, penetrating into the interior and then ionized. The barrier to be crossed by the ions is mainly caused by the repulsion of the external positive ions of the metallic lattice. This barrier is of the same order of magnitude as the work function of the ions. It is thus more probable that at lower temperatures neutral atoms only are able to penetrate into the metal as the barrier for neutral corpuscles is much smaller. Experiments with hydrogen and deuterium have confirmed the existence of a barrier for the penetration of these gases from the surface to the interior of copper. At high temperatures ions may be able to penetrate and we may thus at high temperatures have a quite other order of magnitude for the absorption by various metals than at lower temperatures, especially as it may be difficult for an atom to penetrate into certain metals on account of its »size« whereas it may be possible to the ion.

When at higher temperatures atoms with an ionization potential less than the work function of a surface strikes the surface, adsorption is produced and atoms will evaporate from the surface in the ionic state. This ability of the surface to cause ionization has been proved over and over again by experiments. Such direct proof cannot be ascertained with regard to atoms (or molecules) with ionization potentials larger than the work function. There is however much evidence to show that *the ability to cause ionization extents beyond the height of the work function* although it is difficult or, may be, impossible to produce an emission of ions on account of the ability of the positive ion whose ionization potential is greater than the electronic work function of the surface to capture an electron even at some distance from the surface. There is on the other hand much indirect proof. Brewer[23], for instance, showed that the photo-electric emission curves for iron on which nitrogen,

hydrogen or ammonia has been adsorbed can be duplicated exactly by those obtained from pure iron on which potassium ions have been deposited. The work function is affected by the adsorption and Brewer shows that the treshold potential for the iron used is, when placed in

Ammonia	3,1	volts
Nitrogen	4,4	»
Hydrogen	4,5	»
Vacuum	4,8	»
0,01 per cent of Oxygen in Nitrogen	5,4	»

That the work function is affected by the adsorption suggests that the adsorption is of electrical nature and, that the emission curves when ammonia, nitrogen and hydrogen are adsorbed can be duplicated by those obtained when potassium ions are deposited indicates that ammonia, nitrogen and hydrogen are adsorbed as positive ions notwithstanding that their ionization potentials are higher than the work function of iron. That the presence of oxygen increases the work function indicates that oxygen is adsorbed as negative ions mainly. When potassium ions are deposited on iron the emission is proportional to the concentration of the ions when the fraction of the surface covered is small. Similar proportionality does not exist when the mentioned gases are adsorbed and Brewer suggests that the sensitivity is lowered by the presence of neutral gas particles. *This view accords with the mentioned intermittent ionization.*

That the photoelectric sensitivity of the metals is decreased by the typical catalytic poisons such as hydrocyanic acid, hydrogen sulphide and carbon monoxide suggests that the poisons are adsorbed as ions although their ionization potentials are higher than the work function of the metals.

It has also been demonstated that calcium, strontium, or barium reduces the work function of tungsten in the same manner as potassium, cesium or rubidium although the ionization potential of these metals is higher than the work function of tungsten.

As it has been proved without any doubt that gases with an

ionization potential above the work function of the metal are present in the metal as ions, the metal has a certain power of ionization larger than its work function and, if the metal has such power, why should not that external region which is the surface not have the same.

CHAPTER III.

ACTIVATED ADSORPTION.

It has been observed that there can be a considerable difference in the modes adsorption takes place on a surface at low temperatures and at high. The low temperature adsorption being instantaneously and without a considerable heat of adsorption whereas at higher temperatures the adsorption takes place with increasing velocity when the temperature is raised. From the velocity at various temperatures an *activation energy of the high temperature adsorption* can be calculated. Taylor has therefore termed such adsorption »*activated adsorption*«. The heat of adsorption in activated adsorption is higher than in the low temperature adsorption.

Experiments of Williams have shown that a surface of manganous oxide adsorbs hydrogen in a form without considerable ability to react below 273°K. Above, the hydrogen is reactive and it is suggested that it is adsorbed as atoms. The low temperature adsorption has a heat of adsorption not higher than 0.1 volt and the high temperature adsorption has a heat of adsorption exceeding 0.9 volt. The hydrogen adsorbed below as well as above 273°K is recoverable by evacuation. The adsorption at 580°K is much greater than that at 195°K indicating, when ionic adsorption in accordance with Postulates A and B is considered, that (i) the suggested atoms are formed at the higher temperatures as the lower ionization energy of the hydrogen atom than that of the molecule will produce an increased adsorption with increasing temperature, (ii) elevated

temperature yields activated molecules with a decreased energy of ionization, or (iii) *that a raise in temperature increase the ability of the surface to cause ionization.* Williams further demonstrates that the adsorption is not instantaneous but takes place with increasing velocities with increase of temperature.

Taylor states that a slow adsorption of hydrogen on zinc oxide occurs from $273^{\circ}K$ upwards. At 400 mm pressure the adsorption at $273^{\circ}K$ is 0.14 cc on one gram of the oxide after 1345 minutes, at $383^{\circ}K$ 0.36 cc after 1200 minutes and at $457^{\circ}K$ 0.36 cc after 45 minutes and 0.7 cc after 1200 minutes. The activation energy amounts to 0.6 volt and the heat of adsorption to about 0.9 volt. Below $273^{\circ}K$ the adsorption reaches equilibrium instantaneously with no activation energy and with a heat of adsorption of 0.05 volt, one cc being adsorbed at $83^{\circ}K$ and 0.15 cc at $195^{\circ}K$. The low temperature adsorption seems to be a van der Waals' adsorption increasing with decreasing temperature. At a higher temperature the adsorption is activated.

A delay in adsorption is produced in case a surface adsorbs atoms, compounds or excited molecules only produced by molecular collisions in the gas phase, viz. the surface is able to ionize the atoms, compounds or excited molecules but not the molecules in their normal state. The adsorption will then increase with the time and to a certain degree with increasing temperature. *A delay in adsorption is produced also if the ionization of a molecule requires that the molecule is for a certain time exposed to conditions able to cause ionization.* At low temperatures a molecule approaching the surface is for a longer time close to the surface than at higher temperatures but, *if a raise in temperature increases the ability of the surface to cause ionization more rapid than the time the molecules are close to the surface is decreased, a raise in temperature will increase the velocity of adsorption.* The activation energy calculated in the usual manner is thus not an expression of the true energy of activation, and it is hence *necessary that a firm distinction is drawn between those temperature effects causing alterations in the power of ionization, and those effects which depends on ac-*

tivation of molecules only. »Activated adsorption« can then only indicate that a temperature dependence is involved.

Taylor and Sherman[25] use the ortho-, para-hydrogen interconversion to correlate adsorption and chemical change at surfaces as a specific effect of surfaces existing in this interconversion analogeous to that obtained in chemical reactions. In the transformations where the ratio ortho-para hydrogen is adjusting itself to the equilibrium corresponding to the temperature of the catalyst atomic adsorption has been assumed and Taylor and Sherman conclude from experimental data that the interconversion is not induced by van der Waals' adsorption but is always associated with an activated adsorption of hydrogen. Studies were made of the capacity of surfaces to induce the change from normal (3 ortho-: 1 para-) hydrogen to »liquid air equilibrium« (1 ortho-: 1 para-) hydrogen at liquid air temperature. At higher temperatures ($193^\circ K$ and upwards) studies were made of the capacity of surfaces to induce the reverse change from 1 : 1 to 3 : 1 since, from $193^\circ K$ upwards, the equilibrium hydrogen is substantially 3 ortho-: 1 para.

At liquid air temperature adsorption of the van der Waals' type is able to cause ortho- para hydrogen interconversion when the surface is paramagnetic in nature. Activated adsorption is poison for such interconversion. At higher temperatures the conversion is, however, associated with the activated adsorption. When this adsorption is yielded by ionization the interconversion is caused directly by the ionization or by a dissociation furthered by the ionization, after which the atoms recombine at random.

Eyring and Polanyi in discussing the reaction $H_{2\ para} + H = H_{2\ ortho} + H$ estimate the energy of activation of the reaction on the assumption that in the molecule the atoms are separated by 0.76 Å and, when the third atom approaches, the potential energy of the molecule is increased until all three atoms are 0.96 Å apart. The reaction then takes place. If the molecule is ionized the force keeping the molecule together will be reduced and the energy of activation will thus decrease. The activation energy of the conversion of parahydrogen to the equilibrium mixture at raised temperatures is over 50,000 calories although the heat of conversion

of one form to the other is 329 calories only at 0°K. As the activation energy is of the same order of magnitude as the dissociation energy of hydrogen ions it throws some light on the mechanism involved in the conversion taking place at surfaces.

Activated adsorption and catalytic ortho-para hydrogen interconversion shows that the activated adsorption of hydrogen on zinc-cromium oxide, zinc oxide, manganeous-cromium oxide and copper oxide-chromium oxide sets in at about 273°K and on alumina at 573°. Taylor and Strother[24] confirmed that this is the case for zinc oxide. White demonstrated that activated adsorption of hydrogen on nickel is traceable at 83°K, on platinium at 195°K. Experiments mentioned by Benton[22] show further that the activated adsorption of hydrogen on iron sets in between 90° and 195°K. Frankenburger and Hodler[26] showed that tungsten adsorbs nitrogen weakly at low temperatures. Frankenburger demonstrated that the activated adsorption of nitrogen on tungsten sets in at about 293°K. Benton[22] proved that a similar adsorption of nitrogen on iron takes place at 273°K. On nickel the activated adsorption should according to Benton and White[27] begin between 98° and 173°K, and according to Taylor and Strother[24] the activated adsorption of carbon monoxide on copper sets in at about 273° and on iron at 195°. Drake and Benton[28] have found that hydrogen shows an instantaneous van der Waals' adsorption on silver which is small even at 90°K. Above 470°K activated adsorption occurs. The mentioned experiments show that the *minimum temperature at which a traceable activated adsorption sets in is a characteristic feature of activated adsorption.* Activated adsorption, contrary to van der Walls's adsorption, should thus be due to an *ionization which sets in at the surface in question above a certain temperature.* By the following table is given a few of such minimum temperatures T_o.

Table I.

Adsorption of	Surface	T_0 °K
H_2	Ni	83
H_2	Pt	195
H_2	Fe	90 — 195
H_2	ZnO	273
N_2	Fe	273
N_2	W	293
N_2	Ni	98 — 173
CO	Ca	273
CO	Fe	195

Beebe, Low, Wildner and Goldwasser[29] were able to show that equal amounts of deuterium and hydrogen are adsorbed on copper at 0—2 mm pressure and 195°K. Considering equation (4) that may be interpreted as $m_{H_2} S^2_{H_2}$ being equal to $m_{D_2} S^2_{D_2}$. The ionization potential of the hydrogen molecule is 15.37 volts and of the deuterium molecule about 15.40 volts. As $m_{D_2} = 2m_{H_2}$, A of equation (1) should then be about unity. Considering equation (2) the velocity of hydrogen adsorption must hence be larger than that of deuterium at the temperature and pressure in question. Beebe, Low, Wildner and Goldwasser confirmed by experiments that this is the case. They found furthermore that at 270°K hydrogen is more strongly adsorbed, but at 300°K the adsorption was less strongly. Considering dissociation at higher temperatures and the formation of atomic ions, the adsorption of hydrogen at higher temperatures must be less if the adsorption of the two gases is equal when molecular adsorption takes place at lower temperatures, as the difference in ionization potential for the atoms is less than for the molecules. (The ionization potential of the hydrogen atom is 13.54 volts and of the deuterium atom 13.54 + 0.004 volts as the Rydberg constant for H is 109677.76 and for D 109707.56).

CHAPTER IV.

ADSORPTION AND CATALYSIS.

As activated adsorption is predominant in the case of surfaces which are catalytically active, it has been suggested that adsorption causes catalysis; but how this catalytic action is produced has been unexplained. A quite different state is arrived at when the activated adsorption on, and catalysis at, the active surfaces are taken as two parallel phenomena both produced by an ability of the surfaces to cause ionization.

Chemical combination between atoms is due to the tendency of the electrons in these atoms to take up more stable groupings than those possible as long as the atoms are separate. In combination the atom hence takes up or loses electrons in the outer valency shell in such manner that if possible a stable octet group as found in the inert gases is formed. Sodium having one valency outside a closed group of eight electrons will thus, in combination with chlorine having an outer group of seven electrons, lose one electron to the chlorine atom. In this transfer of an electron sodium becomes a positively charged ion and acquire a stable electronic octet group, whereas chlorine becomes a negatively charged ion with a similar stable electronic group. The compound NaCl is thus held together by the electrostatic attraction between the two ions. In the regrouping of electrons a transfer of one or several electrons is, however, not always required as it is possible that an electron can be shared between two atoms so that the stability of both is increased. We have thus valency bonds, based on a transfer of electrons, called

electrovalency, and the bonds of covalency found in non-ionised molecules, that is based on the sharing of electrons.

The mechanism of chemical reaction of molecules is depending on rupture of one or several of the bonds by which radicals (atoms) of the single molecule are kept together. Such rupture of a covalent bond may be symetrical whereby two neutral radicals are formed, or unsymetrical causing the formation of two opposite charged ions. *The mechanism of gaseous reaction depends normally on the symetrical rupture of bonds and it is not suggested in this book that ionization caused by a surface should change this mechanism.* Rupture may, however, in many cases be a too fierce expression to use if it implies that the radicals are parted by violence as the may be a changing over only from one configuration to another, not involving actural dissociation but only an internal separation of the radicals during the molecular collision leading to reaction.

The velocity of a chemical reaction is usually proportional to $e^{-E/kT}$, where E is the energy of activation. This energy is used to »stretching« the bonds, whereby the radicals of a reacting molecule is brought into a position facilitating the formation of new molecules. If by the introduction of a surface, an electric field, ions or electrons into a reacting system, the energy of activation is lowered, the velocity of reaction will be increased. *The introduction of a surface, an electric field, ions, or electrons has then acted as a catalyst.*

In discussing the energy of activation Hinshelwood[57] summarizes the present view on the energy of activation of chemical reaction, and he staes that the forces between two atoms are made up of two parts: an electrostatic part, the Coulomb force, and a force known as the exchange force, a force similar to that which would come into play if the electrons of two atoms were to preserve always certain definite phase relations to one another in their movements. In molecular formation the exchange force is the more important. He further states that if XZ is a molecule with its atoms at the normal equilibrium distance apart and Y is an atom at a great distance, the energy changes which occur as Y is brought up to the molecule and as Z subsequently recedes to an infinite di-

stance, leaving YX as a molecule, can be estimated and it can be calculated that intermediate configurations will possess a greater energy than the initial or final ones. If the reaction shall occur an »energy pass« must be climbed. *The minimum height of this pass is the energy of activation.* Quantum mechanics show that passage over the pass is not always necessary as there is a probability that passage over the pass can be avoided, Hinshelwood, however, emphasizes that such probability is very small when the energy barrier is high, and therefore that the normal process of passage over the energy barrier may for all practical purposes be more important and that the quantum mechanical leakage effect probably does not play a very large part in determining rates of reaction. The same will apply to the *catalytic reactions at surfaces* and, if a molecule XZ is ionized close to a surface, the energy pass which must be climbed if an YX molecule shall be formed is decreased, viz: *the energy of activation is decreased by the ionization taking place close to the catalytically active surface.*

A molecule bound together by electrovalency and a molecule with co-ordinate covalency giving raise to some negative charge on one radical and a corresponding positive on another possess an electrical dipole moment equal to the product of the charges on the ions and the distance between the centres of the charges. A covalent molecule will have a zero dipole moment as long as its electrons are arranged symetrical round the nuclei. An electric field may, however, induce a dipole moment. There is thus strong electric fields round electrovalent compounds, whereas the electric forces are more or less neutralised within a covalent compound. *External electric forces will thus attack electrovalent compounds more easily than the covalent and, when an electrovalent compound is dissolved in a solvent of high dielectric constant, the two ions of the compound will separate.* Interaction between ions of various dissolved electrovalent compounds is thereby made possible.

If a molecule A with an energy of ionization I_A is ionized, the ion formed is able to ionize a molecule B with an ionization potential I_B if $I_A \geqq I_B$. The ion A^+ and a molecule B are thus able to form a complex $(AB)^+$ during the possible movement of an

electron from A to B taking place in collision of A and B. If an ion B^+ collides with A and $I_A > I_B$, such movement is not possible and a complex cannot be formed. When the complex $(AB)^+$: is formed the reacting molecules are brought into a position facilitating the formation of new molecules. *The ionization has thus acted catalytic and the state, surface, etc. producing the ions has acted as a catalyst.*

A reaction between two molecules is thus facilitated when the molecule with the highest ionization potential is ionized. If a reaction at a surface is assumed to be furthered by ionization it is required

- *(i)* *that the molecules with the highest potential of ionization are present during interaction as adsorbed ions* and
- *(ii)* *that the molecules with the lower ionization potentials are in a neutral state when the collisions leading to reaction take place.*

If the molecules with the highest ionization potential are ionized the molecules with the lower potentials will also be ionized, the conditions (i) and (ii) can thus only be fulfilled in case

- *(iii)* *that the ionization is intermittent.*

In a reaction $2\,MA \dashrightarrow (MA)'_2 \dashrightarrow M_2 + A_2$ the formation of the complex $(MA)'_2$ require that MA is excited in collision to such an extent that association is made possible. If one of the colliding molecules is ionized this association is facilitated and thus the reaction. Such reactions are therefore accelerated by catalysts being able to ionize the molecules intermittently.

When an ion collides with a neutral molecule of a reacting system, the electrons of the molecule may be influenced in such manner that they are caused to drift from their normal position, a change in reactivity is then produced but, only when the energy gained in neutralising the ion is larger than the ionization potential of the reacting molecule so that a transfer of an electron from the molecule to the ion is possible, the reaction is accelerated.

The electronic drift may, however, in certain cases be enough as several compounds will polymerise, for instance, when clusters of molecules are formed round ions.

Catalysis of reactions amongst covalent molecules is thus furthered if the molecules most difficult to ionize are ionized or, what has the same effect, that ions with an ionization potential larger than the ionization potentials of the reacting molecules, are brought into the reacting system. We have thus that, if a hydrogen ion H^+, i. e. a proton, collides with a molecule having an ionization potential less than 13.54 volts, an electron will move from the molecule to the ion. Water, for instance. with an ionization potential of 12.9 volts will hence form the ion $(H_3O^+)'$ in collision with a proton. This ion may again react with a molecule A with a low energy of ionization and a reaction takes place as follows:

$$A + (H_3O^+)' \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; (AH_3O^+)'$$
$$(AH_3O^+)' \longrightarrow B + C + H,$$
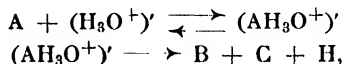
where $(AH_3O^+)'$ is an intermediate reactive complex of the reacting substances. In the process a proton has in reality furthered the reaction $A + H_2O \longrightarrow B + C$. During the reaction an electron has been transferred to the proton and anything able to produce protons will in this case act as a catalyst and the condition for the catalytic reaction to take place is that *an electron is caused to move from products with a low energy of ionization to products with higher and from them to the catalyst.*

Acid catalysis taking place in solution is based on the formation of a fugitive complex from a molecule and a proton and a subsequent decomposition of this complex. This is quite similar to the above mentioned process, the usual description is only a little different as a proton is said to be »transferred« from an acid, A, to a molecule, M, as in

$$M + A \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; MH^+ + B$$
$$MH^+ \longrightarrow$$
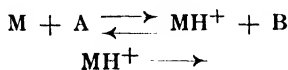
In the acid hydrolysis of cane sugar, S, the process should be

$$S + H^+ \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; SH^+ \longrightarrow$$
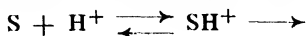
In the catalysis caused by bases, a molecule, MH, is said to give up a proton, namely

$$MH + B \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; M + A,$$
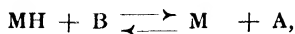
and in the decomposition of nitramine catalysed by bases the process should be

$$O_2NNH_2 + OH^- \; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \; O_2NNH + H_2O$$
$$O_2NNH \; \longrightarrow \; N_2O + OH^-.$$
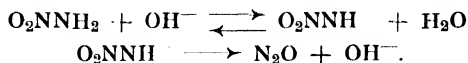
These examples show that a transfer of a proton takes place with the result that a *charged intermediate fugitive complex* is formed. In acid and basic catalysis the rate determining step of the process is the formation of this complex. *At surfaces able to cause ionization the rate determining step will also be the formation of an intermediate charged complex of an ion and a molecule with a subsequent decomposition of the complex.*

The intermittent ionization suggested producing a strong adsorption of molecules on metallic surfaces attempts to keep the molecules in a zone close to the surface, the zone termed the »*positive zone*«. Ionization, however, does not influence the movements of the molecules (ions) parallel to the surface. The adsorbed molecules may therefore act as a two dimensional gas. In this gas, which is partly ionized, collision between the molecules and the ions produces chemical reactions, just like collisions in ordinary gases. As the number of collisions increases by the adsorption, the effect caused by a catalytic surface is due to *(i) a lowering of the energy of activation, and (ii) an increase in the number of active collisions.*

The velocity of a catalytic reaction depends on the total number of collisions between molecules with a joint energy exceeding a certain value E. This number is proportional to $e^{-E/kt}$ and to the adsorption or

$$\frac{p}{\sqrt{T}} \; e^{(^{1}/_{2} \, m \left(\frac{d}{c}\right)^2 S^2 - E)/kT}$$

The velocity depends furthermore on the desorption proportional to

$$p \sqrt{T} \; e^{-m \left(\frac{d}{c}\right)^2 S^2/2kT}$$

The catalytic reaction hence requires that the temperature shall be above a certain value if the reaction is to take place with a considerable velocity and, when $\frac{1}{2}m \left(\frac{d}{c}\right)^2 S^2 > E$, that the pressure will have to be increased when the temperature is enlarged.

The dissociation of nitrogen, oxygen and hydrogen requires the following energies (D)

N_2	$\longrightarrow$ 2N	11.4 volts,
O_2	$\longrightarrow$ 2O	7.1 » ,
H_2	$\longrightarrow$ 2H	4.4 » ,
CO	$\longrightarrow$ C + O	10.0 » .

By electronic impact ions are produced in the gas phase when the following energies (I_m) are free to be used

N_2	$\longrightarrow$ N_2^+	16.7 volts,
O_2	$\longrightarrow$ O_2^+	14.0 » ,
H_2	$\longrightarrow$ H_2^+	15.37 » ,
CO	$\longrightarrow$ CO^+	15.0 » .

The dissociation of molecular ions uses (D^+)

N_2^+	$\longrightarrow$ $N + N^+$	9.1 volts,
O_2^+	$\longrightarrow$ $O + O^+$	6.5 » ,
H_2^+	$\longrightarrow$ $H + H^+$	2.6 » ,
CO^+	$\longrightarrow$ $C^+ + O$	7.0 » .

The ionization of the atoms requires (I_A)

N	$\longrightarrow$ N^+	14.50 volts,
O	$\longrightarrow$ O^+	13.56 » ,
H	$\longrightarrow$ H^+	13.54 » .

Ionization of nitrogen, hydrogen, carbon monoxide thus decreases the energy of dissociation. Savard[30] calculates the energy of dissociation of a molecule A_2 or AB_p to be $2n(I_m - I_n)$ or $2nI_m - \Sigma n_a I_a$ respectively where $2n$ is the number of binding electrons of one shell, n_a the number of electrons furnished by the atom A for this shell, I_m the first ionization potential of the mole-

cule, and I_a that of the atom (provided that in AB_p the number of linking electrons is even, and they are in one envelope). The energy of dissociation of an ion A_2^+ is $(2n - 1)$ $(I_m - I_a)$. It is thus made feasible that ionization will decrease the energy of dissociation of molecules of the type A_2 although the mentioned formula gives only an approximation.

Considering what is mentioned above, the ability to cause ionization must be larger than the ionization potential of nitrogen (16.7 volts) at surfaces able to further the formation of ammonia in a mixture of nitrogen and hydrogen. Many catalysts are able to do so and Os, Mo, Fe, Ni, Co, Mn and W have been used with excellent results, whereas platinum is only able to cause a slow reaction. The ability of platinum should therefore be about 16.7 volts at the temperatures in question and of Os, Mo, Fe, Ni, Mn and W larger. That lithium and cerium produce ammonia is not due to catalysis as a compound of the metal used and nitrogen is produced, and it is such intermediate compound which combine with hydrogen and yields ammonia. That the formation of ammonia by use of lithium and cerium is not a catalytic process is demonstrated by the customary processes as in a catalytic reaction a mixture of hydrogen and nitrogen is passed over the contact substance, whereas nitrogen and hydrogen are passed separately over cerium or lithium one of the gases following the other.

When hydrogen is adsorbed as positive ions on a metal surface the mobile conduction electrons of the metal will concentrate as close to the ion as possible and a strong adsorption is produced. *A positive ion is* thus, *held to the whole of the metal by the electron gas of the metal and it is in no way held to any single ion of the metal.* When on the other hand, oxygen or the halogens having electron-affinity form negative ions on the surface, the electron concentration about the single ion will decrease. *A negative ion will* thus *be attracted by the neighbouring positive metal ions* and we can speak about a *surface oxide or halide.*

The hydrogen molecule is dissociated on surfaces of several incandescent metals; amongst such there is tungsten heated to 1500°K. This dissociation is caused by collisions of a hydrogen

ion and a neutral molecule. If on the other hand tungsten is first placed in oxygen of low pressure *negative* oxygen ions are produced. Hydrogen is thereby kept away from the surface and will not be dissociated. If the oxygen pressure is reduced to such extend that the film covering the surface becomes incomplete, hydrogen molecules are enabled to reach the surface in such manner that ionization occurs and water will be formed.

When a catalyst is poisoned this means that molecules (or atoms) with relatively low energy of ionization are adsorbed by the surface and thereby form an obstacle to the adsorption of the reacting products. This is in accordance with practical results. That in gas reactions the deterioration of nickel, for instance, is diminished by insertion, prior to the nickel catalyst (prior with regard to the flow of gases), of a copper catalyst capable of arresting most of the poisons means that the ability to cause ionization is greater for nickel than for copper. When molecules having electron-affinity are adsorbed they can also act as poisons.

Pure copper causes several kinds of hydrogenation but its activity is not great. Its ability to cause ionization must hence be about the same as the ionization energy of hydrogen. Copper adsorbs hydrogen but if its surface is poisoned the adsorption is easily abolished.

Amongst the energies of ionization of organic compounds can be mentioned:

CH_4	13.7 volts,
C_2H_4	11.5 » ,
C_2H_2	12.3 » ,
C_6H_6	9.6 » ,
CO	15.0 » ,
CO_2	14.3 » ,
HCN	14.8 » .

As the dissociation and hydrogenation of C_2H_2, C_2H_4 and CH_4 in the presence of catalysts are able to give a picture of the catalytic effect the following examples will be mentioned. C_2H_2 dissociates without a catalyst being present at temperatures above 1070°K, and carbon, hydrogen and some methane are produced; the me-

thane formation is due to the hydrogen formed causing a reduction of the C_2H_2. At 870°K polymerisation occurs. C_2H_4 is dissociated at 1120°K and polymerisation takes place at 870°K, for CH_4 the dissociation occurs at 1270°K. Moissau and Moureu showed that C_2H_2 is polymerised, dissociated and hydrogenated in the presence of Ni, Fe and Co, and the dissociation takes place with such a velocity that incandescense is produced, resulting in the total decomposition of the acetylene. Platinum also show this effect but to a weaker degree but copper will on the contrary have to be heated to 510°K before polymerisation takes place. C_2H_4 is polymerised in the presence of Ni and Co at 570°K; the velocity being slowest with Co; Pt and Cu having an inconsiderable effect. With Ni also Sabatier and Senderens showed that destructive incandescence can be produced. Ni and Co dissociate CH_4 at 770°K. Ni hydrogenates C_2H_4 in the presence of hydrogen and heat is liberated; platinum causes the same action but to a smaller extent, and copper requires heating to 400°K if hydrogenation is to be effected. Ni, Co, Pd, and Pt hydrogenate C_2H_4 at ordinary temperature; copper requires 450°K. If such catalysts are arranged in accordance to their catalytic power exhibited we get in accordance with Postulate A the following succession of their abilities to cause ionization:

Ni, Co, Fe Pd and Pt > Cu,
Ni > Co > Pt and Cu,
Ni > Pt > Cu.

As they are all able to cause hydrogenation their ability to cause ionization must be above or equal to 15.37 volts. In this connection it must be borne in mind that surfaces able to ionize the hydrogen are also able to ionize the organic compounds in question. This succession is in accordance with the order of sequence stated in the case of the formation of ammonia where

Os, Mo, W, Fe, Ni and Mn > 16.7 volts;

Adsorption of hydrogen on copper showed

Hg < 15.37 volts and Cu about or just above 15.37 volts.

If acetylene, water vapours and hydrogen pass a zinc oxide catalyst at 650°K a compound of acetylene and water is produced, acetylene and water are ionized by 12.3 and 12.9 volt-electrons respectively, hydrogen at 15.37 volts. If the mixture thus produced passes over nickel at 470°K ethyl alcohol is formed. Considering Postulate A the ability to cause ionization of zinc oxide is therefore below 15.37 volts but above 12.9 volts. If ammonia, acetylene and hydrogen pass over the zinc oxide catalyst at 620°K a compound of acetylene and ammonia is produced which on a nickel catalyst heated to 420°K or 500°K is hydrogenated to ethylamin. The ability of zinc oxide must therefore be above 12.3 volts as the energy of ionization for acetylene and ammonia is 12.3 and 11.1 volts respectively. It is of interest to notice that substituting water with ammonia reduces the necessary temperature of the zinc oxide catalyst.

In the presence of nickel, carbon monoxide and hydrogen mainly produce methane when the temperature varies from 423°K to 553°K and the pressure is 150 atmospheres (equation I). If a lower pressure is used, and the temperature lies between 573°K and 673°K methanol is produced when the catalyst contains zinc (zinc oxide) (equation II). In the presence of copper and the temperature is 573°K to 673°K formaldehyde is preferentially produced (equation III).

(I) $CO + 3H_2 \xrightarrow{Ni} CH_3OH,$

(II) $CO + 2H_2 \xrightarrow{Zn} CH_4 + H_2O,$

(III) $CO + H_2 \xrightarrow{Cu} CH_2O.$
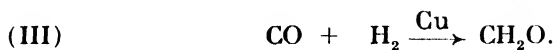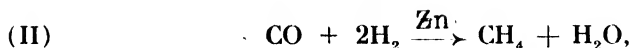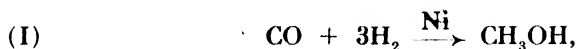
Considering Postulate B the ability to cause ionization of nickel must be larger than that of zinc (zinc oxide), which again must be larger than that of copper, as hydrogen has a higher energy of ionization than carbon monoxide. If the ability of copper is about the same as the ionization energy of hydrogen, a hydrogen molecule adsorbed on copper will, practically speaking, be surrounded by molecules of carbon monoxide, and formaldehyde will be the pro-

duct most probably formed. On the zinc catalyst the hydrogen adsorption must be relatively larger for methanol formation to be possible. On nickel the adsorption of hydrogen will be especially strong, methane formation is therefore favoured. Pt, Co, Pd, and Fe also favours the formation of methane. If a zinc-chromium catalyst is used ether and ethylene are produced besides methanol: $2CH_3OH = (CH_3)_2O + H_2O$ and $2CH_3OH = C_2H_4 + 2H_2O$, which shows that methanol is adsorbed. If the catalytic surface has patches able to ionize hydrogen and the remaining part is able to ionize products with a lower energy of ionization than hydrogen, compounds of formaldehyde and water, for instance, are produced on such less active parts. Such compounds may be hydrogenated off the boundaries of the most active patches, and higher alcohols, aldehydes, ketones, acids and oily products are produced. The products from which »Synthol« is produced in accordance with Fischer[31] contain such mixture and they are yielded by carbon monoxide and hydrogen in the presence of an iron catalyst to which several metals unable to adsorb hydrogen have been added. Pure iron gives, like nickel and manganese, methane only. By such a hydrogenation cobalt showed a lower effect than iron or nickel, and platinum a lower one than palladium. Copper decomposes methanol into methylformate and an addition of zinc oxide to the catalyst of copper alters part of the products of decomposition to formaldehyde, carbon monoxide and hydrogen. This alteration increases with an increased amount of zinc in the catalyst. (Generally zinc oxide is not reduced at the temperatures employed, but in the presence of copper reduction occurs). Similar decomposition is produced by oxide of manganese, but alumina is only able to dehydrate. Latter work by Fischer has shown that a very efficient atmospheric pressure process employing an iron-copper or a cobalt catalyst for the production of liquid fuel from watergas can be established.

The molecule of ethyl alcohol is dissociated into aldehyde and hydrogen (equation IV) when copper or zinc oxide is used as catalyst, and the temperature is 570°K. At the same temperature alumina or tungstic oxide produce ethylene and water (equation V):

$$\text{(IV)} \quad \begin{matrix} CH_2 \\ | \\ H \end{matrix} . \begin{matrix} CH_2 \\ | \\ OH \end{matrix} \xrightarrow{\;Cu\;} \begin{matrix} CH_2 \\ | \\ H \end{matrix} . \begin{matrix} CH \\ | \\ O \end{matrix} + H_2 \;,$$

$$\text{(V)} \quad \begin{matrix} CH_2 \\ | \\ H \end{matrix} . \begin{matrix} CH_2 \\ | \\ OH \end{matrix} \xrightarrow{\;Al_2O_3\;} CH_2 : CH_2 + H_2O.$$

The order of various catalytic oxides used in the last process is

$$MnO > ZnO > Fe_2O_3 > SiO_2 > Cr_2O_3 > W_2O_3 > Al_2O_3.$$
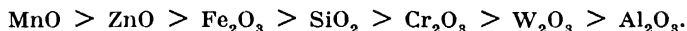
If an iron catalyst is used an increased adsorption of hydrogen takes place and ethane is produced besides aldehyde, as

$$CH_3CHO + H_2 \longrightarrow CH_3CH_3 + H_2O.$$
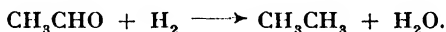
Brown and Travers[32] showed that the removal of hydrogen from carbon is very slow when the carbon has been saturated with hydrogen at 740^0 and then being outgassed for 48 hours but, as soon as methane was admitted it was found possible to recover hydrogen, partly as methane and partly as hydrogen gas. Considering Postulate B methane should thus have a lower energy of ionization than hydrogen, and this is the case as hydrogen is ionized by 15.37 volts and methane by 13.7. Carbon should hence have an ability to cause ionization of 15.37 volts or more. Besides, as shall be shown later, *the enlarged adsorption produce a decrease in the ability to cause ionization* and thus loosens the adsorption.

On a surface of heated platinum nitrous oxide is decomposed as

$$2N_2O = 2N_2 + O_2.$$
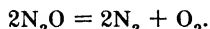
The corresponding homogeneous decomposition demands and activation energy of 2.5 volts. The catalytic reaction only wants about 1.4 volts. Electronic impacts produce ions of nitrous oxide when electrons with an energy of 12.9 volts collide with molecules of nitrous oxide in the vacuum tube. Considering Postulate A platinum should thus have an ability above 12.9 volts, ions of nitrous oxide are then produced when the oxide comes close to the surface of platinum and it is this ionization which should account for the reduced activation energy.
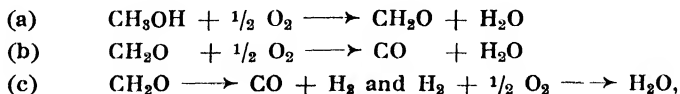
The decomposition of ammonia on a copper catalyst shows that the rate of decomposition varies directly with the partial pressure of ammonia and inversely as that of hydrogen but the rate is independent of the nitrogen pressure. In accordance with Postulate A a copper surface should hence be able to ionize hydrogen but not nitrogen.

The reaction

$$C_2H_2 + H_2O \longrightarrow CH_3CHO$$

takes place on the oxides of Fe, Ni, Cu, Zn and on carbon. As acetylene is ionized by 12.3 volts and water by 12.9 the oxides and carbon must have an ionization ability greater than 12.9 volts. Ammonia and sulphuretted hydrogen poison the reaction. These products are thus adsorbed preferably due to their lower energy of ionization, 11.1 and 10.4 respectively.

When oxygen is adsorbed as negative ions electrons shift from the metal to the oxygen molecule. There is, however, also the possibility that positive oxygen ions are formed but, when a negative oxygen ion is adsorbed the ability of the surface to cause the formation of positive ions is poisoned considerably, the negative oxygen ions will thus be the predominant. The oxygen adsorption causes an increase in the work function of the surface, the surface will hence have an ability to produce positive ions also when the surface has adsorbed oxygen ions although this ability may be weaker than before. When methanol, for instance, is oxidised on platinum 5.2 per cent of formaldehyde is produced. If the reaction takes place on copper 70 per cent is yielded. If the following reactions take place:

(a) $CH_3OH + \frac{1}{2} O_2 \longrightarrow CH_2O + H_2O$

(b) $CH_2O + \frac{1}{2} O_2 \longrightarrow CO + H_2O$

(c) $CH_2O \longrightarrow CO + H_2$ and $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$,

the catalyst able to further (a) only produces most formaldehyde. Copper on which oxygen is adsorbed should thus be able to ionize methanol preferentially.

In the absence of oxygen methanol is dehydrogenated on ZnO,

4*

MnO and copper. The relative rate of evolution of hydrogen at 620°K being 15, 17, 50 and 100 respectively. With more active catalyst, nickel, for instance, a decomposition of the formaldehyde into carbon monoxide takes place.

The contact processes of oxidation are divided into two parts, one during which a catalyst does not enter into »intermediate« compounds, and one where the »carrier« is an oxide which may oxidize the products in question, the »carrier« being simultaneous re-oxidized. The boundary between the two kinds of processes is not always easily fixed, and it is a question if many of the oxidations taking place on the surface of oxides to which oxygen is supplied are not of a purely catalytic character. By catalytic oxidation negative oxygen ions are kept close to the surface. Oxygen may therefore easily poison an oxidation process. As the molecules to be oxidized will have to be ionized by the catalyst the ability of the active surface to cause ionization must when oxygen is adsorbed also be high enough to ionize the molecules to be oxidised. A special reactivity is thus not attributed to the negative oxygen ion. Amongst oxidations taking place on surfaces can be mentioned the oxidation of SO_2 to SO_3 which can be carried out on various oxides and on platinum. The reaction $2SO_2 + O_2 = 2SO_3$ is retarded by sulphur trioxide formed, this is due to the high molecular weight of the trioxide whereby it displaces the dioxide. The sulphur dioxide used will when platinum is employed have to be free from arsenic able to poison the catalyst as arsenic has a great molecular weight and a very low energy of ionization. The poisoning therefore takes place in accordance with Postulate B. Sulphur dioxide is ionized at about 13.1 volts. The catalysts used shall hence in the presence of oxygen and at the temperatures in question have an ability to cause ionization above 13.1 volts. Chromium oxide catalysts are in accordance to Adadurov[33] very active and produce up to 97 % conversion of SO_2 to SO_3 at 720 — 730°K. Vanadium oxide catalysts produce 93 % conversion at 570°K and in accordance to Brodovitsch and Golovko[34] 98—99 % at 670—680°K. Iron oxide catalysts are effective also. Platinum is a very efficient catalyst able to produce 99 % of the equilibrium amount of the trioxide rapidly at tempe-

ratures from 670 to 870ºK. Iridium will at equal conditions produce
26 to 84 % of the yield produced by use of platinum and palladium
1 to 39 % thereof. When the mixture of the dioxide and air is
passed over a catalyst of the platinum type it will have to be
free of impurities, especially arsenic. Vanadium oxide catalysts and
to a certain extent iron oxide catalysts are not poisoned by arsenic.
Arsenic pentoxide is in itself a catalyst for the conversion, it is
thus possible that on the vanadium oxide catalyst the arsenic is
able to build up an active new surface instead of inhibiting the
activity of the substratum oxide. Bodenstein and Fink[35] showed
that the reaction velocity was approximately proportioned to the
sulphur dioxide pressure, but it was inhibited considerably by the
SO_3 pressure, indicating that the ionization potential of SO_3 is less
than that of SO_2.

Ammonia is oxidised on platinum at about 720 — 770ºK with
a yield of up to 98 %. The oxide catalysts giving a much lower
yield. It has, however, been possible to prepare catalysts of iron
oxide to which bismuth has been added which is nearly able to
compete with platinum. In accordance with Marmier[36] the metal
catalysts have the following order af activety, Pt > Cr > W > Mo
> Mn > Fe, or the opposite order as in hydrogenation. The reason
is that the efficient hydrogenation catalysts will decompose the
ammonia.

Benton and Elgin[37] showed that the reaction velocity of the
oxidation of hydrogen on silver was proportional to the partial
pressure of hydrogen, whereas the water formed retarded the reac-
tion. Silver does not ionize hydrogen but, as shall be shown in a
later chapter, silver on which oxygen is adsorbed may, however, be
able to do it.

Of oxides causing oxidation may be mentioned the oxides of
cobalt, manganese and zinc having about equal activity. The pure
oxides are very active but mixtures of various oxides also show a
considerable effect. Amongst such mixtures may be mentioned one
containing 60 % MnO_2 and 40 % CuO. Active oxides adsorbs gases
just like the metals. The adsorption on one gram of MnO_2 is at
300ºK 6.17 cc carbon dioxide, and 1.26 cc carbon monoxide, which

is in conformity with the higher molecular weight of the dioxide and its lower energy of ionization; (CO_2 14.3 volts; CO about 15 volts). The adsorption on other active oxides seems similar. Considering the Postulates A and B the oxides of manganese, cobalt and zinc should have an ability to ionize of just above 15 volts, that of tungsten and alumina below 15 volts.
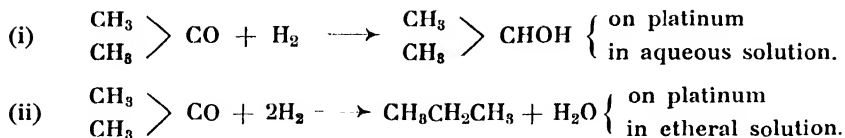
When a mixture of carbon monoxide and hydrogen burns on a catalyst of copper or platinum, the rate of monoxide to hydrogen burnt on copper is much larger than on platinum. Considering Postulate B copper on which oxygen is adsorbed should thus have a lower ability to cause ionization than platinum. The combustion of the mixture on a *copper catalyst* is further regulated by the *admixture of palladium* to the catalyst and the ratio of monoxide to hydrogen brunt increases as the catalyst is changed from one of pure copper up to the catalyst contains 0.2 per cent of palladium. The proportion of monoxide adsorbed on the catalytic surface increases at the same time. The lattice of the catalyst is simultaneously increased. In a later chapter it will be shown that such increase lowers the ability of the surface to cause ionization.

Green[38] show that toluene is oxidized on platinum, CuO, NiO Co_2O_3 and Fe_2O_3 to benzaldehyde and benzoic acid and that the effect of these catalysts is greater than that of Mo_2O_3 and W_2O_3.

In homogeneous reactions increased pressure furthers processes causing a diminution in volume. Such a diminution does not affect the reaction on a catalytic surface directly. All the same, as the diminution means that fewer molecules are formed able to take up the space of the catalytic surface, processes followed by a decrease in volume should have a possibility of being specially adapted to catalysis but, if the resulting products, when the Postulates A and B are considered, have a low energy of ionization the diminution of volume will not be of any help. Dissociation should, for the same reason, be furthered by low pressure but in this case also the energy of ionization may have a predominant influence.

When acetone is hydrogenated with platinum as a catalyst isopropyl alcohol is formed if the reaction takes place in aqueous

solution. In etheral solution the product yielded is propane. The two reactions are:

(i) $\dfrac{CH_3}{CH_8} \Big> CO + H_2 \longrightarrow \dfrac{CH_3}{CH_8} \Big> CHOH \begin{cases} \text{on platinum} \\ \text{in aqueous solution.} \end{cases}$

(ii) $\dfrac{CH_3}{CH_3} \Big> CO + 2H_2 \dashrightarrow CH_8CH_2CH_8 + H_2O \begin{cases} \text{on platinum} \\ \text{in etheral solution.} \end{cases}$

The ionizations potential of acetone is 10.1 volts, of water 12.9, ether 13.6 and hydrogen 15.37 volts. The relative amount of hydrogen adsorbed will thus be less in aqueous solution and the reaction takes place in accordance with (i). With an increased adsorption in the presence of ether the reaction shifts to (ii) with isopropyl alcohol as a possible intermediate compound.

In accordance with Noyes[30] two electrons of the oxygen atom of acetone must be classified as nonbonding having ionization potentials not differing much from that of the oxygen atom, two are antibonding with ionization potentials lower than that of the oxygen atom. Of the four bonding electrons two are probably weakly and two strongly bonding having ionization potentials higher than either the oxygen or the carbon atom (I. P. 14 and 11.22 volts). The lowest ionization potential found to be 10.1 volts corresponds probably to the removal of an electron which will, in reality, not be associated entirely with the oxygen atom but belongs to the group as a whole.

It is thus probable, but not at all given, that ionization of acetone will increase its reactivity. That the electron removed in ionization belongs to the group as a whole makes it obvious that the CO group is kept close to the surface during adsorption on a surface having an ability to cause ionization larger than 10.1 volts. When hydrogenation shall take place the ability shall be above 15.37 volts, and the hydrogenation will take place in collision of a hydrogen ion and a neutral acetone molecule keeping in mind that the ionization is intermittent. A complex

$$\dfrac{CH_8}{CH_8} \Big> CO \quad \overset{\frown}{} H_2^+ \longrightarrow \left[\dfrac{CH_8}{CH_8} \Big> COH_2^+\right]'$$
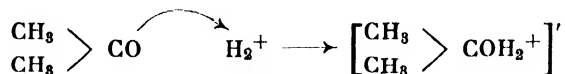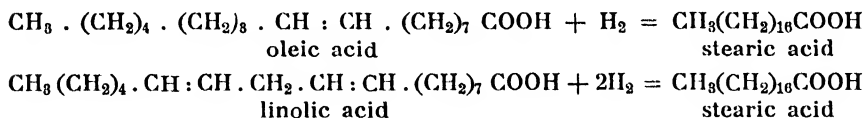
is thus formed and a regrouping to the alcohol will take place before or during the neutralisation by an electron.

Ethylene having an ionization potential of 11.5 volts is hydrogenated on nickel, platinum, palladium, copper, etc. Morris and Reyerson[40] showed that platinised and palladised silica gels show marked activity as catalysts over a considerable range of temperatures. Palladium at 330° K being more active than platinum at the same temperature and both had more activity at 330°K than copper at 500° K. The relative adsorption of ethylene on copper being much larger than on platinum and palladium. The ability to cause ionization should thus be in the order: $Pd > Pt > Cu$.

When the glycerides of unsaturated fatty acids or the fatty acids themselves are hydrogenated the double bonds can be saturated and the carboxyl groups reduced. The catalyst employed is usually nickel, but even a catalyst like copper may be employed. The hydrogenation proceeds step by step. First linoleic, linolenic and other highly unsaturated acids are saturated and then any oleic acid present. Considering oleic and linolic acid we have:

$$CH_3 . (CH_2)_4 . (CH_2)_3 . CH : CH . (CH_2)_7 \: COOH + H_2 = CH_3(CH_2)_{16}COOH$$
<div align="center">oleic acid   stearic acid</div>

$$CH_3 (CH_2)_4 . CH : CH . CH_2 . CH : CH . (CH_2)_7 \: COOH + 2H_2 = CH_3(CH_2)_{16}COOH$$
<div align="center">linolic acid   stearic acid</div>

In linolic acid we have thus three possible adsorption centres, in oleic acid two only. Linolic acid is thus adsorbed preferentially and hence hydrogenated in preference to oleic acid. The carboxyl group is not affected at lower pressures due to a certain inactivity of this group ascribed to "resonance" causing the linked atoms to come nearer together than should be expected in accordance with ordinary structural theory. The link is hence strengthened, and we may thus have two strong adsorption centres only (at the double bonds) and one weak in linolic acid, and one strong and one weak in oleic acid. At high pressure the carboxyl group is reduced, and the double bonds are largely unattacked. When the pressure is increased the possibility of the molecules lying flat on the surface, as during the attraction to the surface at two or more

points, is decreased as the compression will cause the molecules to stand at a fairly steep angle to the surface. Hydrogenation of the double bonds is thus reduced and the carboxyl group only has a chance of being adsorbed and thus hydrogenated.

That the carboxyl group has a certain inactivity is further demonstrated by the hydrogenation of fumaric and maleic acids on platinum and palladium as succinic acid is formed:

$$\begin{matrix} CH \ . \ COOH \\ \| \\ CH \ . \ COOH \end{matrix} + H_2 \longrightarrow \begin{matrix} CH_2 \ . \ COOH \\ | \\ CH_2 \ . \ COOH. \end{matrix}$$

As the hydroxyl group also has a certain resistivity, oleic alcohol is first hydrogenated to a saturated alcohol and then to the corresponding saturated hydrocarbon.

Benzene having an ionization potential of 9.6 volts is hydrogenated to cyclohexane in the presence of nickel, cobalt, iridium, platinum and palladium. The activity of the catalysts decreasing from nickel to palladium. Even copper can be employed as a catalyst. When phenol is hydrogenated cyclohexanol is produced. In the same manner pyridine is reduced to piperidine. Sabatier and Murat[41] showed that benzhydrol is hydrogenated to diphenyl methane on nickel:

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CHOH + H_2 = \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} > CH_2 + H_2O$$
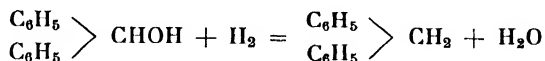
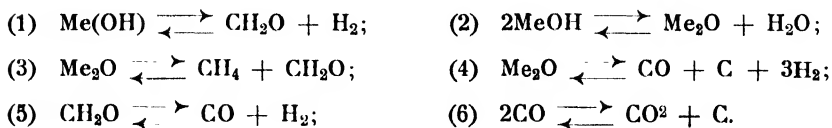In this case the adsorption takes place at the CHOH group.

Carbon disulphide (I. P. 14.4 volts) is hydrogenated to hydrogen sulphide and carbon when nickel is employed as a catalyst. The oxides of nitrogen (I. P. of NO 9,4 volts and of N_2O 12.9 volts) are reduced when nickel, platinum, copper, etc. are used. Nitrobenzene is in the same manner reduced to aniline but, as the process taking place on nickel is too violent, the weaker catalyst palladium and copper being more suitable.

In the hydrogenation of coal, tars and mineral oils products with a low energy of ionization are present and thus products easily able to poison the usual hydrogenation catalysts. Relatively

weak catalysts are therefore employed and the hydrogenation is assisted by the presence of sulphur or hydrogen sulphide[42] added in the free state or formed in situ. The sulphur is in many cases present in the product to be hydrogenated. For tars a vanadium oxide catalyst is very efficient in the presence of sulphur. In the hydrogenation of coal the sulphides or oxides of iron, cobalt, molybdeum, etc. are employed. Even a tin-plated iron catalyst can be used. These catalysts are quite different from the usual hydrogenation catalysts and are unable to ionize hydrogen. The hydrogenation depends hence on a reaction between the sulphide (I. P. 10.4 volts) and the organic matters having ionizations potential about or below 11 volts. By such process sulphur is set free able to react with hydrogen without the presence of a catalyst. Hydrogen sulphide is in this manner supplied for the catalytic hydrogenation. Sulphur hence act as a carrier of the hydrogen.

Hydrogen sulphide (I. P. 10.4 volts) poisons the reaction between acetylene (I. P. 12.3 volts) and water (I. P. 12.9 volts) and Bredig[43] showed that in the decomposition of hydrogen peroxide on platinum, hydrogen sulphide (I. P. 10.4 volts) destroyed the activity of the catalyst to a much larger degree than hydrogen cyanide (I. P. 14.8 volts). Molecules with a low energy of ionization are thus the most poisonous, i.e. they are adsorbed preferentially. It is further found that the more active catalysts are more exposed to poisoning than those with a lower activity and that poisons are more active at low than at high temperatures. A given reaction may also be self-poisoning. The temperature will therefore have to be above a certain value before the reaction will take place with a considerable velocity.

Kuss[44] studying the decomposition of Methyl alcohol found that the following reactions take place on metalic surfaces:

(1) $Me(OH) \rightleftarrows CH_2O + H_2$;

(2) $2MeOH \rightleftarrows Me_2O + H_2O$;

(3) $Me_2O \rightleftarrows CH_4 + CH_2O$;

(4) $Me_2O \rightleftarrows CO + C + 3H_2$;

(5) $CH_2O \rightleftarrows CO + H_2$;

(6) $2CO \rightleftarrows CO_2 + C$.

(1) and (2) take place on nearly all metallic surfaces even aluminium and silver. Iron is initially good for (1) but deteriorates rapidly owing to deposits of carbon produced by (5) and (6). The ionization potential of methyl alcohol is about 12 volts and of carbon monoxide and dioxide 15 and 14.3 volts respectively. The ability of the iron surface to cause ionization is thus larger than that of aluminium and silver.

Baladin, Marushkin and Ikonikov[45] found that the reaction velocities of dehydrogenation of isopropyl alcohol and cyclohexanol on copper were the same. It is hence assumed that both molecules are attracted to the copper surface by the $>CHOH$ group. It is hence this group that is ionized by the surface.

Baladin[46] was able to measure the activation energy of the dehydrogenation on various catalysts and found with the catalysts mentioned below:

		E in Kgcal
Piperidine	Pd	16.2
»	Pt	19.9
Decahydronaphthalene	Ni	< 10.0
»	Os	10.0
»	Os	16.5
»	Pt	19.0
Cyclohexane	Ni	9.7
»	Ni	13.7
»	Pd	15.3
»	Pt	18.0

The catalysts with the highest ability of ionization should require the lowest amount of energy of activation. In accordance with the measurements of Baladin the ability of the mentioned catalysts should decrease from nickel to platinum.

When methyl oleate is hydrogenated on nickel the hydrogenation is much more rapid that when nitrobenzene is reduced on the same catalyst but, as shown by Green,[47] if a mixture of nitrobenzene and methyloleate is hydrogenated, the nitrobenzene is reduced preferentially. If the ionization potential of nitrobenzene is lower than that of the methyl oleate, nitrobenzene must be adsorbed

preferentially to the oleate, the preferential hydrogenation is thus produced. When the products are reduced separately the hydrogen adsorption will in the presence of nitrobenzene be less than in the presence of the oleate, the hydrogenation og nitrobenzene will therefore be slower than that of methyl oleate.

When Nyrop[1] in 1930 proposed that ionization plays an important part in contact catalysis and when this theory was further developed in the first edition of this book nothing was known of the chemistry of heavy hydrogen. It has thus been of especial interest to follow the now rapidly accumulating experimental facts with regard to the heavy hydrogen isotope, deuterium, which was first prepared by Washburn and Urey[48] in 1932 by electrolysis under suitable conditions of water. It was discovered that when ordinary water is electrolysed light hydrogen is liberated in preference to deuterium so that deuterium will remain preferentially to light hydrogen in the water left after electrolysis. Oliphant[49] observed in 1933 that when hydrogen is kept in contact with water for a few months an *exchange of atoms* occurs between the water and the hydrogen. Horiuti and Polanyi[50] found that this exchange reaction was catalysed by platinum black. Taylor and Diamond[51] showed that the reaction was furthered also at higher temperatures by zinc oxide and chromium oxide. Horiuti and Polanyi suggested that the catalytic exchange of atoms between water and hydrogen is due to an ionization of hydrogen just as in the electromotive process taking place at an electrode. In acid solution the exchange reaction is very rapid. The reaction is

$$H_2O + HD \xrightleftharpoons{\quad} HDO + H_2.$$
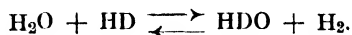
According to Horiuti and Polanyi the hydrogen (HD) is split into ions at the surface of the catalyst and the ions go into solution. At the same time ions arriving from the solution will form hydrogen on the catalyst. The exchange is thus made possible. In accordance with the theory under consideration in this book *hydrogen and water is ionized intermittently at the surface of the catalyst and thus adsorbed. Hydrogen ions has thus the chance of combin-*

ing with water so that the exchange is made possible. The reaction should be

$$HD^+ + H_3O \rightleftharpoons [HDH_2O^+]' \dashrightarrow HDO^+ + H_2$$
$$HDO^+ + \varepsilon = HDO.$$
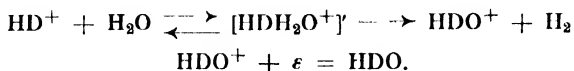
The exchange should thus readily take place on the hydrogenation catalysts at temperatures where these catalysts are able to ionize hydrogen. As hydrogen ions are present in water a catalytic inactive surface like glass will concentrate some hydrogen and deuterium ions at its surface. Such inactive surfaces will thus be able to further the exchange somewhat, but the velocity will be slow.

In electrolysis of water hydrogen ions as well as deuterium ions will concentrate at the cathode. Now the ionization potential of deuterium is slightly larger than that of hydrogen, there is thus a possibility that the reaction

$$D^+ + H_2O \rightleftharpoons DH_2O^+ \rightleftharpoons HDO + H^+$$
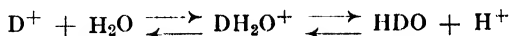
will have a chance of proceeding more rapidly from the left to the right than in the opposite direction. To this comes that of the two reactions

(i) $\quad H^+ + H \longrightarrow H_2^+$

(ii) $\quad H^+ + D \dashrightarrow HD^+$
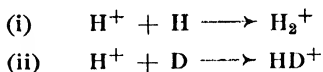
(i) only is possible. A separation of the two isotopes is thus favoured. The efficiency of separation is expressed by the "separation coefficient" indicating how many times the light hydrogen is liberated more readily than deuterium. This coefficient depends on current density and p_H but also on the metal of the electrode. Bell and Wolfenden[52] showed that the coefficient for copper and platinum cathodes was 5.3, but for nickel 4.3. This indicates that, *with increasing catalytic activity of the cathode, the process of separation is counteracted.* The process

$$H_2^+ + HDO \dashrightarrow H_2O^+ + HD$$

is caused by catalytic active cathodes, a counteraction is thus

feasible. When the electrolyte becomes enriched with respect to deuterium, processes like this will produce an increase in the amount of deuterium in the liberated hydrogen.

At liquid air temperature adsorption of the van der Walls' type is able to cause ortho-para hydrogen interconversion when the surface is paramagnetic in nature. At higher temperatures the conversion is yielded by the ionization caused by the catalyst employed. The ionization acts either directly, or indirectly by a dissociation furthered by the ionization, after which the atoms recombine at random.

In accordance with Kalckar and Teller[53] the transition probability between ortho- and para-states is zero. There are, however, two ways of inducing an ortho-para transformation. The one consists in introducing a perturbation which depends both on the spin and on the position of the nuclei. The other consists in dissociating the molecules after which the atoms are recombined. This are the two ways mentioned with regard to the action of surfaces.

The weak adsorption of low temperatures of the van der Walls' type on surfaces paramagnetic in nature is poisoned by activated adsorption of the hydrogen. Activated adsorption thus poisons the conversion of ortho- to para-hydrogen at liquid air temperature. The possible reactions at higher temperatures taking place on catalytic active surfaces should be

$$H_2^+ + p\text{-}H_2 + \varepsilon \longrightarrow [H_2H_2^+] + \varepsilon \longrightarrow o\text{-}H_2 + H_2.$$

Farkas[54] showed that the velocity of the reaction between HD and water vapours on a platinum catalyst is about one tenth of that of the hydrogen interconversion. The rate of the exchange is independent of the water pressure and increases nearly linearly with the deuterium pressure. This indicates a stronger adsorption of the water than of the hydrogen so that the exchange is in reality poisoned by adsorbed water.

Gould, Walker, Bleakney and Taylor[55] showed that mercury, pyrex and soft glass-surfaces do not promote the reaction between H_2 and D_2 at room temperature. Charcoal not at liquid air tem-

perature, whereas nickel promotes the reaction at as low a tempe-
rature as 80°K. The reaction is thus quite similar in its require-
ments to the catalyst as hydrogenation.

Taylor and Jungers[56] have been able to prove that the exchange
reaction between deuterium and ammonia occurs on iron catalysts
as employed in the synthesis of ammonia, even at room tempera-
ture. They further showed that the exchange does not occur on
quarts even at 570° K. The ammonia-deuterium exchange on iron
being a slower process than the hydrogen-deuterium exchange on
nickel.

In the reaction

$$D_2^+ + H_2 \longrightarrow [D_2H_2]^+ \longrightarrow HD^+ + HD$$
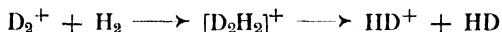
the difference in ionization energy of the reactants is so small that
the process will proceed unimpeded.

In the reaction

$$DH^+ + NH_3 \longrightarrow [DHNH_3]^+ \longrightarrow NDH_2^+ + H_2$$

the ionization potential of ammonia (11.1 volts) is so much lower
than that of hydrogen and deuterium (15.37 and 15.4 volts) that
the ammonia is adsorbed preferentially. Ammonia has thus a
poisonous effect able to decrease the velocity of the exchange.

The catalytic hydrogen-deuterium exchange preceeds also more
rapid than the deuterium-water exchange. Also in this case the
low ionization potential of water (12.9 volts) will cause a preferen-
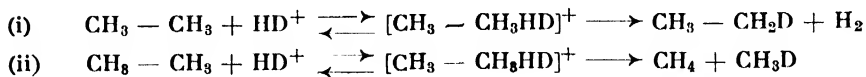tial adsorption that impedes the reaction.

Farkas[54] investigated the exchange of hydrogen atoms between
deuterium and ammonia on an iron catalyst and found that the
rate of exchange is independent of the concentration of ammonia
and increased approximately according to the square root of the
deuterium concentration. This agrees with the view expressed above
with regard to the influence of the lower ionization potential of
ammonia. It was further showed that the relative rates of the
orthopara conversion of hydrogen and deuterium and of the reaction
$H_2 + D_2 = 2 HD$ are as $5 : 2 : 7$. As deuterium has a somewhat
higher ionization potential than hydrogen, the hydrogen conversion

will be more rapid than that of the deuterium conversion. All three reactions are much faster than the deuterium-ammonia exchange being "poisoned" by the ammonia. This is confirmed directly as the presence of ammonia inhibits the ortho-para conversion. The "energy of activation" of the deuterium-ammonia exchange is 15 cals., of the conversions and the deuterium-hydrogen exchange 8-9 cals. only. This also is in agreement with a poisonous effect of the low ionization potential of the ammonia.

Tucholski and Rideal[58] showed that when ethylene is reduced with hydrogen and deuterium on a nickel catalyst the reaction rate with hydrogen is larger than with deuterium up to about 440° K, when the speeds become identical. The difference between the energies of activation of the two processes decreased at the same time. In this case the ethylene with an energy of ionization of 11.5 volts will act as poison and the poisonous effect will be largest for the reaction with deuterium having the highest ionization potential. As the poisonous effect will decrease with increasing temperature the velocity of the two reactions will hence approach each other. Klar[59] found furthermore that the velocity of hydrogenation of ethylene is on iron lowest with deuterium at temperatures between 270° K and 370° K. At higher temperatures (measured up to 450° K) it is highest with deuterium. By increasing the temperature the activity of the catalyst increase buth the adsorption decrease, a maximum velocity of the reaction will hence be passed during the increase. Klar found that the maximum velocity occurred at about 420° K with deuterium and at about 390° K with hydrogen. A reversal in the hydrogenation is thus caused.

Taylor, Morikawa and Benedict[60] showed that when deuterium or hydrogen was adsorbed and exchanged with ethane produced without any appreciable amount of ethane having reacted with the deuterium (hydrogen) to form two molecules of methane at 411° K exchange proceeded quantitatively, while the production of methane sets in at 423° K. The two reactions are

(i) $CH_3 - CH_3 + HD^+ \rightleftharpoons [CH_3 - CH_3HD]^+ \longrightarrow CH_3 - CH_2D + H_2$

(ii) $CH_3 - CH_3 + HD^+ \rightleftharpoons [CH_3 - CH_3HD]^+ \longrightarrow CH_4 + CH_3D$

In (i) the C—H bond is involved, in (ii) the C—C bond. When (i) shall proceed the C—H bond shall be ionized by the adsorbed deuterium (hydrogen) ion. At lower temperatures when the adsorption of ethane is large the molecules stand at a fairly steep angle to the surface, ionization of the C—H bond is thus most possible although the ionization potential for the C—C bond is lower. At higher temperatures when the adsorption decreases and the ability of the surface to cause ionization is enlarged so that the time the ethane molecule is ionized by the surface is prolonged, whereby the ionization may drift to the C—C bond, the molecules will have an increased possibility of lying flat on the surface. Reaction with the C—C bond is then favoured.

Taylor, Morikawa and Benedict[61] also showed that methane undergoes exchange with D_2, CD_4 and D_2O on active nickel catalysts. At 457° K the rate of reaction decreased in the order $CD_4 > D_2 > D_2O$. In the reaction $CH_4 + CD_4$ none of the reacting molecules are adsorbed with any considerable preference. In $CH_4 + D_2$ methane is adsorbed preferentially due to its lower ionization potential, and in $CH_4 + D_2O$ it is D_2O that for the same reason is adsorbed preferentially. When such preferential adsorption occurs the rate of reaction is decreased.

Eley and Polanyi[62] demonstrated that in the catalytic exchange of hydrogen with water and alcohol on platinum the rate determining step is a splitting of the hydrogen molecule. It is suggested that the products of dissociation of hydrogen cannot be homo-polar hydrogen atoms, but must be ions or atoms in a strongly polarised state, e.g. participating in a Pt-H linking. This suggestion is not in contradiction to the general theory of ionization at catalytic active surfaces as set out in this book.

CHAPTER V.

THE CATALYTIC SUCCESSION OF SURFACES.

In the preceding chapters the ability of several surfaces to cause ionization has been estimated. *Table 2* is a synopsis of such estimates. By $A > B$ is indicated that the adsorption on or the activity at a catalyst A is stronger than on B, or that the energy of activation of a given process is less when A is employed. The ability of A to cause ionization should then be larger than that of B. When T_0, then minimum temperature at which a given process is determinable, is lower for the adsorption of a gas on A than on B it indicates also that the ionizing ability of A is larger than that of B. q_0 of the table is the ionization potential of the molecules the catalyst is able to ionize. Considering *table 2* we obtain *table 3*, giving the succession of the catalysts corresponding to a diminishing ability to cause ionization.

Table 2.

Process	Catalyst	T_0	q_0
		°K	volts
Adsorption of H_2 (J. P. = 15,37 volts)	Ni	83	> 15.37
	Pt	195	> 15.37
	Fe	90—195	> 15.37
	ZnO	273	> 15.37
	Oxides	> 400	> 15.37
	Ni $>$ Pd $>$ Cu		> 15.37
Adsorption of N_2 (J. P. = 16.7 volts)	Fe	273	> 16.7
	W	293	> 16.7
	Ni	98—173	> 16.7

Process	Catalyst	T_o	q_o
		°K	volts
Adsorption of CO (J. P. = 15 volts)	Cu	273	> 15.0
	Fe	195	> 15.0
Ethylene (J. P. = 11.5 volts) is adsorbed more strongly than hydrogen (J. P. = 15.37 volts) on Cu, Ni and Pt, but relatively most on Cu	Ni; Pt > Cu		> 15.37
Adsorption of H_2 (J. P. = 15.37) and CH_4 (J. P. = 13.7 volts)	Cu > C		> 15.37
Adsorption of CO (J. P. = 15 volts) and H_2 (J. P. = 15.37 volts)	Ni > Pt > Cu		> 15.37
	Cu		15.37
Adsorption of H_2O (J. P. = 12.9 volts) on Hg inhibit photoeffect, H_2 (J. P. = 15.37 volts) does not	Hg		15.37 > Hg > 12.9
Adsorption of D_2 (J. P. = 15.4 volts) and H_2 (J. P. = 15.37 volts)	Cu	195	> 15.4
Ortho-para hydrogen conversion	Fe		> 15.37
	ZnO		> 15.37
	Al_2O_3		> 15.37
	Ni > Cu > C		> 15.37
Ortho-para deuterium conversion	Fe		> 15.4
Decomposition of H_2	W		> 15.37
Catalytic exchange of atoms between hydrogen (J. P. = 15.37 volts) and water (J. P. = 12.9 volts)	Pt		> 15.37
Hydrogenation of aldehydes to alcohols	Ni; Cu		> 15.37
Hydrogenation af CS_2	Ni; Fe; Co		> 15.37
Hydrogenation of oils	Ni; Co; Pt		> 15.37
Hydrogenation of naphthalene	Ni; Fe;Pt; Pd		> 15.37
Methanol synthesis	ZnO; MnO		> 15.37
	ZnO — Cr_2O_3		> 15.37

5

Process	Catalyst	T_0	q_0
		°K	volts
Hydrogenation of organic sulphur compounds	Cr_2O_3; MoO_3; Cr_2O_3		> 15.37
Hydrogenation of coal in the presence of hydrogen sulphide (J. P. = 10.4 volts)	WO_3; Fe_2O_3; WO_3; CoO		> 10.4
Hydrogenation of CO	Ni; C		> 15.37
Hydrogenation of amylacetylene to amyl acetate to heptane	Cu ⎫ Ni > Cu Ni ⎭		> 15.37
Hydrogenation of organic products	Ni; Co; Cu; Fe Ni > Co Ni > Fe		> 15.37 > 15.37 > 15.37
Hydrogenation of C_2H_4	Pd > Pt > Cu		> 15.37
Synthesis of NH_3 from N_2 (J. P. = 16.7 volts) and $3H_2$ (J. P. = 15.37 volts)	Os; Mo; Fe; Ni; Co; Mn; W Fe > Pt Os > Pt		> 16.7 > 16.7 > 16.7
Synthesis of acetaldehyde from acetylene (J. P. = 12.3 volts) and water (J. P. = 12.9 volts)	Hg		> 12.9
Decomposition of NH_3 (J. P. = 11.1 volts)	Cu Os > Pt		> 11.1 > 11.1
Decomposition of nitrous oxide (J. P. = 12.9 volts)	Pt		> 12.9
Decomposition of CO (J. P. = 15)	Ni > Cu		> 15.0
Organic decompositions	Ni; Co; Fe; Pd; Pt; > Cu Ni > Co > Pt; Cu		
Decomposition of formic acid vapours	Au; Ag		

Process	Catalyst	T_o	q_o
		^oK	volts
Decomposition of ethyl alcohol into aldehyde and hydrogen (dehydrogenation)	Cu; ZnO; ZnS.		
Decomposition of ethyl alcohol into ethylene and water (dehydration)	Al_2O_3; W_2O_3.		
Dehydrogenation of hydrocarbons)	Ni; Fe; Co; Cr; Cu Fe_2O_3; MoO_3; WO_3; MoS; CoS.		
By contemporary organic dehydration and dehydrogenation the formation of hydrogen decreases, and that of water increases in the order of catalysts	$MnO > ZnO > F_2O_3 > SiO_2 > Cr_2O_3 > W_2O_3 > Al_2O_3$		
Oxidation of CO	$\begin{cases} Co_2O_3 > CuO > \\ Fe_2O_3 > V_2O_5 > SiO_2 \\ Al_2O_3 \\ Cr_2O_3 \\ Fe_2O_3 \end{cases}$	< 800 < 700 < 600	
Oxidation of methanol	$\begin{cases} Pt > Cu \\ Ag; Cu—Ag; Ag—Pt \end{cases}$		
Combustion of a mixture of H_2 and CO	$Pt > Cu$		
Oxidation of NH_3 (J. P. = 11.1 volts)	$Fe > Mn > Mo > W > Cr > Pt$.		
Oxidation of SO_2 (J. P. = 13.1 volts)	Pt; V_2O_5; Fe_2O_3; CuO; Cr_2O_3 and oxide mixtures		
Oxidation of paraffins	V_2O_5; MoO_3; WO_3; $ZnO — Cr_2CrO_8$.		
$CH_4 + H_2O \longrightarrow CO$ (or CO_2) + H_2 (J. P. of CH_4 = 13.7 volts)	Ni; Fe; Co		

Process	Catalyst	T_o	q_o
		$^\circ K$	volts
$C_2H_2 + H_2O \longrightarrow CH_3CHO$			
$\quad C_2H_2 + H_2O \longrightarrow CH_3COCH_3$			
$\quad$((J. P. of $C_2H_2 = 12.3$ volts)			
$\quad$of $H_2O = 12.9$ volts)	Fe_2O_3; $ZnO - Cr_2O_3$; MoO_3		
Production of heavy hydrogen by electrolysis of water	$Ni > Pt$; Cu		
Exhange between H_2			
$\quad$(J. P. $= 15.37$ volts) and D_2			
$\quad$(J. P. $= 15.4$ volts)	Ni	80^0	> 15.4
	C	$> 120^0$	> 15.4

Table 3.

Succession of the metals corresponding to a diminishing ability to cause ionization.

Metals	Ability to cause Ionization	Ionization Potential
Ni Os Fe Mn Co W Pd Pt	Able to ionize N_2	16.7
Zn Cu C	Able to ionize H_2	15.37
Ag		
Hg	Able to ionize water	12.9

The succession of the oxides becomes

$$Mn > ZnO \text{ (about 15.37 volts)} > Co_2O_3 > CuO > Fe_2O_3 > V_2O_5 >$$
$$SiO_2 > Cr_2O_3 > Al_2O_3.$$
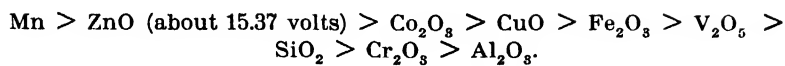
The succession of the catalyst is determined at equal temperatures above the minimum temperatures for the processes employed in evaluating the ability.

CHAPTER VI.

## ELECTRONIC BOMBARDMENT-REACTIONS.

When the electric discharge passes through a gas mixture chemical reaction among the components of the mixture is facilitated. In atmospheric oxygen ozone is produced under the influence of the silent discharge and several "silent discharge reactions" are known such as dissociation of water vapours, condensation of hydrocarbons, formation of active nitrogen and oxidation of sulphur dioxide.

These reactions are due to ionization of the gases by the discharge.

When electrons are passed through a mixture of hydrogen and nitrogen Buch-Andersen[63] demonstrated that a formation of ammonia begins at an electron-velocity of approximately 17.5 volts, the velocity of reaction increasing rapidly with enlarged electron-velocity. Electron energies corresponding to the dissociation work of nitrogen or hydrogen not being enough to cause reaction.

If electrons having energies of more than 16.7 volts collides with molecules of nitrogen the corresponding ions are formed such ions will react with hydrogen as the ionization potential of hydrogen is 15.37 volts or less than that of nitrogen. Brett[64] demonstrated that an electron-velocity of 17 volts is required in case electronic impact shall produce ammonia in a mixture of nitrogen and hydrogen. As mentioned by Gill[65] the values can easily be estimated somewhat too high as in the use of the ordinary arrangements for measuring of electronic velocities an electron loses velocity due to space charge. Wansbrough-Jones[66] showed that 17 electron volts

are required if oxidation of nitrogen shall take place. In this case the reaction should be

$$N_2^+ + O_2 \longrightarrow (N_2O_2)^+ \longrightarrow 2NO$$
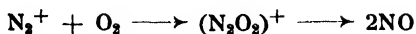
the free positive charge being neutralised by an electron. The process does not take place if only oxygen ions are formed by 14.1 electron-volts.

It can thus be estimated that ammonia is not formed in a nitrogen-hydrogen mixture, or nitric oxide in a nitrogen-oxygen mixture, at electron velocities below 16.7 volts. That it is the nitrogen alone and not the hydrogen, or oxygen, which has to be ionized is an expression of a general rule saying that *two molecules will not react with each other by help of electronic impact if the molecule most difficult to ionize is not ionized by the electron. The electron energy shall thus be larger than the ionization potential of the molecule most difficult to ionize.* When an ion of the molecule most difficult to ionize comes into contact with a molecule with a lower energy of ionization, the ion is able to capture an electron from the molecule. The formation of an intermediate fugitive complex is then made possible and thus the reaction between the two molecules.

Besides such reaction in which *exchange of electrons in a given direction* takes place, we have reactions in which molecular clustering about ions leads to polymerisation, for instance. The polymerisation of acetylene by alpha rays is an example of such reactions.

In the glow discharge it has not been possible to ascribe any reactivity to excited molecules and only when the accelerating voltage is high enough to produce ions of the molecules most difficult to ionize chemical reactivity is observed.

In the investigation of Wansbrough-Jones[66] it was, as mentioned, demonstrated that the rate determining step of the oxydation of nitrogen by electronic impact was the formation of nitrogen ions, ionization of the oxygen did not lead to reaction. At 18 volts 50 electrons were required to form one ion and 10 ions to form one oxide molecule. At 25 volts 6.7 electrons per ion and 1.6 ion per oxide molecule, and at 40 volts 2.2 electrons per ion and 1.3 ions

per oxide molecule. The yield is thus increasing rapidly when the accelerating potential is increased.

Brewer and Miller[67] showed that the formation of ammonia in a $3H_2:N_2$ mixture exposed to a low voltage arc is independent of the pressure, except at the lowest values, and that it is directly proportional to the current through the arc. *Synthesis does not occur at arc potentials below the ionization potential of nitrogen.* The rate increases rapidly between 17 and 23 volts, linearly to 50 volts. The maximum rate of synthesis at 0,3 mm pressure in the 19-and 30-volt arc occurs in a mixture containing 83 vol. % nitrogen. The addition of less than 80 % of helium, neon and argon to $3H_2: H_2$ mixtures has only small retarding effects increasing from helium to argon.

(helium: atomic weight 3.99, I. P. 24.4 volts;
neon: » » 20.20, » 21.4 » ;
argon: » » 39.88, » 15.7 » .)

The experimental results indicated that the reaction occurs around N_2^+ and N^+ ions. H_2^+ ions, neutral atoms and excited molecules being relatively inactive. An evaluation of the rate of ions between nitrogen and hydrogen indicates a yield of two molecules of ammonia per N_2^+ ion, below 23 volts and about one molecule of ammonia per N^+ ion. The retarding effect of helium, neon and argon, increasing from helium to argon or with decreasing ionization potential of the admixed gases, indicates that the formation of ions foreign to the purpose slows down the reaction. Brewer and Westhagen[68]) showed similarly that the synthesis in a glow or Geissler discharge was slowed down in a pronounced manner by argon, helium having no effect up to 70 % of the gas. In the synthesis of ammonia in the glow discharge no ammonia is formed in the dark spaces, and maximum reaction is observed in the negativ glow where the electrons are accelerated most.

As to the oxidation of hydrogen in the glow or Geissler discharge, Brewer and Westhagen[68] demonstrated that the reaction was initiated by H_2^+ ions. At higher temperatures it was indicated that O_2^+, N_2^+ and A^+ (admixed) could form effective reaction nuclei.

(I. P. of H_2 15.37 volts, O_2 14, N_2 16.7 and A 15.7 volts). That nitrogen and argon hawing ionization potentials higher than that of hydrogen is able to form reaction nuclei is in conformity to the above mentioned rule as an electron will be able to pass from a hydrogen molecule to a nitrogen or argon ion, and from an oxygen molecule to the formed hydrogen ion, but that oxygen should be able to form a reaction nuclei can only be due to a clustering of molecules round the oxygen ion. Other investigations show, however, that an H_2^+ ion will form two molecules of water after making 20 collisions in a $2 H_2:O_2$ mixture, while an O_2^+ ion will require of the order of 1600 collisions to react.

Harteck and Roeder[83] showed that a glow discharge through a mixture of neon (20 mm pressure) and hydrogen or oxygen (0.5 mm) dissociated the later gases. This is again an example showing how ions of atoms (neon) with a high ionization potential are able to produce reaction among molecules with lower ionization potentials.

In the electronic-bombardment reactions and in the reactions caused by catalytic active surfaces we have thus quite the same condition to be fulfilled, i. e. that the ability of the surface to cause ionization and the energy of the bombarding electrons shall be larger than the ionization potential of those molecules among the reactants most difficult to ionize. In the catalytic reactions we have furthermore that molecules with a low energy of ionization will act as poisons, the same slowing down of the reaction by the presence of molecules with a low ionization potential takes place in the electronic-bombardment reactions.

CHAPTER VII.

THE METALS.

A metal is a solid which is a good conductor of electricity. Metallic conduction gives no products of electrolysis nor polarization and, it is supposed that quasi-free electrons carry the current. As other substances than the metals are able to carry electricity in the same manner the expression »electron-conductors« can be used for all such conductors. In accordance with the *classic theory* of electron-conductors a metal consists of (1) atoms having lost one or more of their valency electrons and (2) electrons — lost by the atoms — free to move among positive ions fixed at the lattice points which neutralise their charges and are formed by the atoms. The electrons set free should behave approximately like a monatomic gas. Such *electronic gas* will contribute to the specific heat of the metal as thermic equilibrium should exist between the gas and the ions of the metal. However, such contribution has not been proved to exist. It was therefore suggested that the kinetic energy of the electrons did not alter with the temperature and *the number of free electrons and their velocities should be due to a contact effect* caused by the nearness of the atoms to each other whereby the velocity distribution should only be a function of the lattice structure. Oppenheimer pronounced that »the ionization potential of metallic atoms is characteristically low, so that the valence electrons will be pulled out easily by the field of neighbouring atoms. If the probability of ionization is large, we shall no longer be justified in associating an electron with a single ion, and in this sense the

valence electrons will be free«. *The kinetic energy of the electrons should thereby be uninfluenced by the temperature and only temperature variations influencing the lattice should indirectly be able to alter the kinetic energy.* Considering systems each consisting of an electron of charge e rotating about a nucleus of charge n_ie, where n_i represents the number of positive charges on the nucleus, and having a kinetic energy E_{kin} of such magnitude that the force of attraction is equal to the centrifugal force.

$$(9) \qquad E_{kin} = \frac{n_i \; e^2}{2 \; r};$$

where 2r is the diameter of orbit. Such systems coming into a distance 2r of each other may be able to exchange electrons with a kinetic energy E_{kin} without any alteration in total energy in case the systems do not influence each other otherwise than neutralizing the forces acting on electrons being in the middle between two nuclei. Such exchangeable electrons will only be part of the whole agglomerate of systems and not bound to certain nuclei, viz: the electrons are »free«. It could be imagined that the mentioned contact effect produced when the atoms of a metal are brought together is yielded in a similar manner. If 2r is the distance between the nuclei of the atoms, a the volume occupied by a gram atom of the metal and N the Avogadro constant $2r = N^{-1/3} a^{1/3}$ and if E_{kin} is in volts,

$$(10) \qquad E_{kin} = 12 \; a^{-1/3} n_i.$$

An electron which once obtained a kinetic energy of this magnitude would to a certain extend have the possibility of being able to pass through the metal without loss in energy. In the mentioned system we have

$$(11) \qquad E_{kin} = -\tfrac{1}{2} \; E_p = -E = W,$$

where E_p is the potential energy of the electron, E the total energy and W the energy required to remove the electron to infinite distance. (E_p is negative as the potential energy is put equal to zero at $r = \infty$). If in another system an energy I is required to remove an electron to inifinte distance an energy $W - I$ is gained

when an electron is transposed from this system to the first. *If every ion of the metallic lattice is taken as a closed system in which there is no room for free electrons -W = E represents the lowest energy the free electrons can obtain and E_{kin} their maximum kinetic energy.* As the metal is made up of electrons influencing each other there is, however, no reason to believe that its electrons will act classically. This example is therefore only giving a very rough picture of what may possible happen. Sir Oliver Lodge explains that electrons are jumping continually from one atom to another, which may be due to influence of quanta of radiation confined in the metal, so that the interior of a metal is not unlike the interior of a star but Sir Oliver pronounces that it is simpler to think of the electrons as continuously free, like the particles of a gas moving among alien obstacles, like a wind blowing through a scaffolding, or a gas obstructed by a porous substance.

Sommerfeld[69] assumes that *valency electrons are effectively free* to move about among positive ions, i. e. atoms of the metal that have lost one or more electrons. He further *applies the theory of gas-degeneration on the electron gas* formed and his calculations show that *the gas only will contribute insignificantly to the specific* heat of the metal — only about k/100 instead of 3k/2 as would be the case if the electronic gas acted as an ordinary gas, (k is the Boltzmann gas constant). Sommerfeld calculates the kinetic energy of the electrons and found that the average energy is much larger than the average energy of the molecules of an ordinary gas. According to the *Fermi-Dirac Statistics* the number of electrons with kinetic energies between ε and $\varepsilon + d\varepsilon$ is

$$(12) \qquad n(\varepsilon)\ d\varepsilon\ =\ \frac{4\pi\ (2m)^{3/2}}{h^3}\ \frac{\varepsilon^{1/2}d\varepsilon}{1 + e^{(\varepsilon\ -\ E)/kT}}$$

where h is Planck's constant, m the the mass of an electron and *E the »maximum« kinetic energy of the electrons.* Sommerfeld showed that

$$E\ =\ \frac{h^2}{8m}\ \left(\ \frac{3n}{\pi}\ \right)^{2/3}$$

or if E is in volts

(13)
$$E = 26 \; a^{-2/3} n_i^{2/3}$$

where a is the volume occupied by a gram atom of the metal, n the number of free electrons per cc of the metal and n_i the number of free electrons per atom. At absolute zero the free electrons have energies up to E, while at higher temperatures a few have energies above E. Nevertheless E is termed the »maximum« kinetic energy of the electrons. When $\varepsilon \ll E$ we have approximately

(14)
$$n(\varepsilon) \; d\varepsilon = \frac{4\pi \; (2m)^{3/2}}{h^3} \; \varepsilon^{1/2} d\varepsilon$$

and when $\varepsilon \gg E$

(15)
$$n(\varepsilon) \; d\varepsilon = \frac{4\pi \; (2m)^{3/2}}{h^3} \; e^{(E - \varepsilon)/kT} \; \varepsilon^{1/2} d\varepsilon \quad .$$

The Fermi-Dirac Statistics is based on the *Pauli exclusion principle*[70] that in an assembly of electrons no two electrons can ever have simultaneously the same set of quantum designations. *When $\varepsilon < E$ most of the possible electronic states are occupied*, while for $\varepsilon > E$ most are empty, viz: the electrons do not influence each other, (14) is hence similar to the distribution law of Maxwell. Fermi[71] treating the atoms as a nucleus surrounded by a degenerate electronic gas of a density

(16)
$$n = \frac{2^{3/2}\pi \; m^{3/2} \; e^{5/2}}{h^3} \; P^{3/2},$$

where P is the potential, indicates that such treatment may possible lead to information on the electronic state of solids. The estimation of the potential gives, however, great difficulties.

In accordance to Sommerfeld the electric conductivity of a metal is

(17)
$$x = c \; E \; 1 \; ,$$

where 1 is the mean free path of an electron. As observed conductivities show that this path must be much longer than the spacing of the lattice of the metal this might be difficult to explain classically. Quantum Mechanics gives however no difficulties as the

space-periodic potential through which the electrons move should not affect them. The free path would thereby be infinitely long and only impurities or thermal perturbations altering the potential affect the movements and hence shorten the free path. This seems confirmed by the effect of small traces of impurities on the conductivity. If it is assumed that an electron does not loose kinetic energy in moving through a space-periodic potential and that only oscillations of the lattice and foreign atoms will disturb the electron in its movements, dissolution of another metal in the conductor will diminish the conductivity whether the conductivity of the added metal is higher or lower than that of the conductor. Perfectly miscible metals like gold and silver, copper and nickel, platinum and palladium or nickel and chromium show a decrease in the conductivity when one of the metals is added to the other, a decrease continuing until a minimum of conductivity is reached after which the conductivity rises to that of the added products. In the case of metals unable to mix perfectly like copper and platinum, aluminium and zinc, copper and silver, etc. the addition of silver to copper, for instance, produce a fall in the conductivity until the copper is saturated by 6 per cent of silver, the fall afterwards decreases as mixed crystals are produced. Such decrease continues until a saturated solution of copper in silver is obtained after which the conductivity increases to that of silver. If two metals only produce mixed crystals a continuous variation of the conductivity from that of the one metal to that of the other is obtained. All such variations can be due to variations in the free path of the electrons. As oscillations of the lattice influence the periodicity of the potential, the temperature of a metal will influence the mean free path and thereby the conductivity, and only when the ions of the metal are at rest a perfectly periodic potential can exist. At the absolute zero of temperature the lattice is however not at rest, infinite conductivity due to an infinitely long free path should therefore not exist. *At high temperatures calculations based on the Sommerfeld theory show that the conductivity is varying as T^{-1}. This is in agreement with experiments.* At low temperatures experiments show that the conductivity increases more rapidly than

T⁻¹ and at very low temperatures the experiments of Kammerlingh Onnes in his cryogenic laboratory at Leyden show that »*supra-conductivity*« is in many cases reached before the absolute zero of temperature. The rapid increase in conductivity at low temperatures can to a certain extend be explained when the Pauli's principle is considered as exchange in energy between the lattice and an electron is made difficult. Supra-conductivity and the effect of a magnetic field applied in case of supra-conducting metals and also the influence of alternate current in case of supra-conductivity at low temperatures are, however, unexplained. Kapitza has, however, mentioned that a magnetic field increases the scattering power of an atom and thus decreases the free path of an electron and thereby the conductivity. Not only metals but a number of borides, carbides, nitrides and silicides become supra-conducting when sufficiently cooled. Even a product like copper sulphate, which, when heated, conducts electricity electrolytically, becomes a perfect conductor when cooled. It is found that the inner part of a conductor in the superconducting state may be non-superconducting and that the adsorption of β-rays, as demonstrated by M'Lennan, emitted by meso thorium and adsorbed by a thin sheet of lead which is gradually cooled from a temperature above to a few degrees below the critical transition temperature of $7.2^\circ K$ (the temperature at which lead becomes supra-conducting) does not show any discontinuity in the adsorption coefficient. This indicates that rapidly moving electrons cannot pass the metal in the same manner as the relatively slow electrons of an ordinary electric current. At the present stage of knowledge *the above mentioned phenomena do not contradict the Sommerfeld theory whereby a certain »maximum« kinetic energy of the free electrons can be calculated as the phenomena seems only to have relation to the free path of the electrons and to the scattering power of the ions of the lattice and not to the distribution of energy among the electrons.*

The body of free electrons inside a metal has been mechanically demonstrated and Sir Oliver Lodge has emphasised that there is hope that some means may be found for counting the number of free electrons.

Considering a conductor in which the valency electrons are free to move with a kinetic energy not larger than E among positive ions fixed at the lattice points which neutralise their charges, such »free« electrons can, as shown by Sommerfeld, be regarded as a degenerate gas capable of expanding. *Electrons will therefore escape through the surface of the conductor* but, as *the conductor is surrounded by a potential barrier,* which barrier is partly built up of a field produced by electrons which have crossed the surface, the electrons cannot leave a zone close to the surface. This barrier, P, is greater than a potential difference which would retard the electrons having the maximum kinetic energy, E, and *the work of emergence of an electron, the »work function«, is*

(17) $\varphi = P - E.$

The potential energy of an electron along a line perpendicular to the surface of the conductor is as sketched in the following diagram.
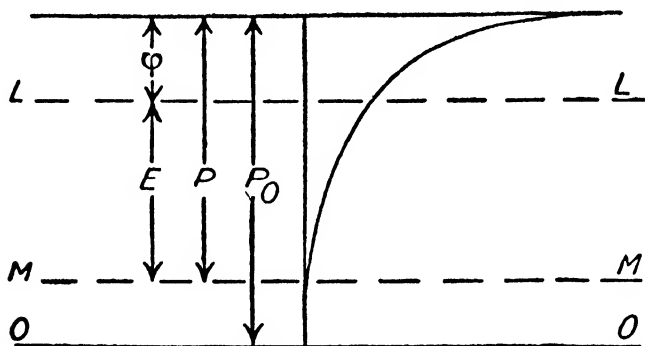
L—L represents the highest level to which an electron can reach by use of the maximum kinetic energy and the energy φ must be supplied to lift the electron from the conductor. *An electron coming from the outside will in moving to the level M—M gain a kinetic energy P. If all levels below M—M are occupied* and most of them above are empty, *an electron cannot fall to a level with a lower energy than that of M—M and if a molecule with an energy of*

ionization J comes close to the surface an energy A = P — J is gained when an electron is brought from the molecule to the level M—M. When the molecule is someway off making an actual collision with the surface of the conductor a *potential hill* forms an obstacle to the electron and, according to classical mechanics, the electron is unable to jump over the hill into the metal without having sufficient kinetic energy to do so. But *in Quantum Mechanics no such barrier is complete as there is a certain chance that an electron will pass through the hill* into a level of energy equal to that of the level left. The electrons have hence an ability to penetrate through a region of »negative kinetic energy«. This effect is called *the tunnel effect.* Gurney[72] has applied this to electrolysis and showed how electrons of higher levels of a conductor A immediately make transition through a potential barrier into a conductor B with lower levels, leaving a positive charge on the surface of A. (This positive charge modifies the potential energy in B, creating new local electron levels).

In accordance to (15) there is some electrons coming from the interior of the metal that will strike the surface with a velocity large enough to overcome the potential barrier. A thermionic current is thus possible. By estimating the number of electrons striking the surface and assuming that the surface of a metal is characterised as a region with a very sudden variation of the potential, that, according to wave mechanics, will cause a reflection of some of the electrons, Fowler and Nordheim[73] deduced the relation

$$(19) \qquad i = AT^2 e^{-\beta/T}$$

for the electron current per unit area of metal surface. $A = 4\pi m \epsilon k^2 D/h^3$ and $\beta = \varphi/k$, where D is the emission coefficient, i. e. the ratio of the number of electrons going through the surface to the number of incident electrons. From the classical theory on metallic conduction Richardson deduced the equation

$$(20) \qquad i = aT^{1/2} e^{-\beta/T}$$

Owing to the overwhelming influence of $e^{-\beta/T}$ it is very difficult

to decide experimentally whether it is the function AT^2 that is correct or $aT^{1/2}$.

Electrons crossing the surface of the metal but unable to over-come the total potential barrier and therefore kept in a zone close to the surface will produce *an electron gas covering the surface*. This gas shall be termed the *»surface-electrons«*. The idea that the surface of a metal is covered by an electronic gas is not new. Oliphant and Moon[74] show, for instance, that the existence of the gas plays an important role in the neutralisation of ions brought into contact with the surface of a metal and that the gas accounts for a simultaneous secondary ejection of electrons. Bartlett and Waterman[75] calculates the density of the electronic gas and show that classical electron distribution exists in the gas at a certain distance from the surface, that the density of the gas is independent of the nature of the conductor and at a given distance is directly proportional to the absolute temperature and, that the mean elec-tron separation distance in a plane parallel to the surface is con-siderably with the distance of the plane from the surface. It is thus a question whether it is permissible to assume that the sur-face is characterised as a region with a very sudden variation of the potential. In the following deduction a less steep potential bar-rier is assumed.

The number of electrons incident on the surface with a kinectic energy of the electron's motion normal to the surface larger than E is

$$(21) \qquad n_s = \frac{4\pi m}{h^3} (kT)^2 .$$

In a distance s off the surface where the electrons have lost an energy E, these electrons produce a gas with a density

$$(22) \qquad n_g = 10 \pi (mkT)^{3/2} h^{-3}$$

Some of the electrons of this electronic gas, *the surface-elec-trons,* will gain such velocity that they are able to cross the re-maining part of the potential barrier. The electronic current thus produced becomes

(23)
$$i = n_g \sqrt{\frac{kT}{2\pi m}}\, e^{-\varphi/kT}$$

$$= \frac{4\pi m k^2 \varepsilon}{h^3}\, T^2 e^{-\varphi/kT}$$

$$= A\, T^2 e^{-\varphi/kT}$$

$$= 120\, T^2 e^{-\varphi/kT}$$

An expression quite similar to (19).

An applied *electric field will be able to pull electrons from the surface-electrons* and thus produce an enlarged electronic current from the surface. When the field able to extract electrons is applied *the density, n_g, of the surface-electrons will increase. The thermionic constant of the T^2 law (equation (23)) will hence increase also.*

Near the outermost zone in a distance $x < s$ the density is expressed by an equation similar to (22), but the density is somewhat larger. Aproximately the distance between the outermost zone and the surface, viz. a plane through the exterior nuclei of the metallic ions, is

(24)
$$s = c_1\, a^{-1/6}\, n_i^{1/3}\, T^{-1/2}$$
and
(25)
$$E/s = c_2\, a^{-1/2}\, n_i^{1/3}\, T^{1/2}$$

where c_1 and c_2 are constants. E/s is an expression for the average field strength at the surface.

In calculating s it has been estimated that the electronic density at the surface is equal to that of the interior of the metal, although the density is somewhat less at the surface and just below. The electrons crossing the surface are thus accelerated sligthly just before the retardation sets in, and P becomes equal to $(E + \triangle E) + \varphi$.

As to the field accounting for φ, this is strongest at distances not much larger than s off the surface, but the strength will decrease as the density of the outermost part of the surface electrons is enlarged, i. e., with raising temperature. A part of φ equal to

(26)
$$\varphi' = \mu\, T^{-3/2}\, \varphi$$

may thus be able to assist in the ionization ($\mu\,T^{-1/2} < 1$). *At high temperatures the ability of a surface to cause ionization is thus equal to E, but at lower temperatures $E + \varphi'$.*

By use of equation (25) the notion »*equivalent temperatures*« with regard to catalytic active surfaces can be defined as the temperatures at which the average field strength is equal at the surfaces. For two surfaces the dependency becomes

$$(27) \qquad \frac{T_1}{T_2} = \frac{a_1\ n_{i_2}{}^{2/3}}{a_2\ n_{i_1}{}^{2/3}} ,$$

where T_1 is the temperature at which the field strength at the surface of a metal M_1 is equal to that at a metal M_2 at a temperature T_2.

When equation (13) is applied and every atom of the metal loses one electron ($n_i = 1$), the value E of table 4 is obtained for the maximum kinetic energy. Now some electrons are more loosely bound to the metallic atoms than the rest, hence it is possible that the single atom will lose so many electrons that a stable electronic shell is left. For iron, chromium, manganese, molybdenum, and tungsten, for instance, there are several possibilities, Z. E of table 4 is hence calculated by use of an average value n_i. By measuring the electronic current from a heated surface the work function, φ_{ex}, of the table is calculated. T_e of the table is the »equivalent temperature« for the various metals at which the field strength is equal to that of nickel at a temperature of 100°K.

It will thus be noticed that the experimentally determinated *ability to cause ionization of table 3 is mostly larger than E but less than $E + \varphi_{ex}$.*

On account of the *tunnel effect* there is a possibility that an electron will make a transition to the metal from a molecule coming close to the surface before actual collision with the surface occurs if the ionization energy of the molecule is less than the difference in potential of an electron placed where the molecule is situated and one at the lowest, not occupied energy level of the metal. The transition may, however, not take place before the molecule is inside the part of the potential barrier which accounts for the work func-

Table 4.

Metal	φ_{ex}	Z	E′	n_i	E	$E+\varphi_{ex}$	T_e
Ni	5.0	4	7.47	4	18.8	23.8	100
Os	—	2	11.60	2	18.4	(23.2)*	93
Fe	4.8	2—6	7.15	4	18.0	22.8	107
Cr	—	2—4—6	6.92	4	17.4	(22.1)	111
Mn	—	3—5	6.77	4	17.1	(21.8)	114
Mo	4.6	4—6	5.83	5	17.1	21.6	123
W	4.5	4—6	5.80	5	16.9	21.4	126
Pd	4.5	4	6.40	4	16.2	20.7	126
Co	4.0	3	7.30	3	15.2	19.2	121
Pt	6.0	4	5.97	4	15.1	21.1	138
Zn	3.3	2—6	5.96	4	15.0	18.3	139
Cu	3.7	1—5	7.10	3	14.8	18.5	130
C	4.1	2	8.50	2	13.5	17.6	128
Al	3.9	3	5.63	3	11.7	15.6	202
Au	—	1—5	5.50	3	11.4	(14.6)	206
Ag	2.9	1—5	5.47	3	11.3	14.2	208
Hg	—	2—6	4.42	4	11.1	(14.0)	214
Pb	3.9	4	3.78	4	9.5	13.4	278
Mg	3.0	2	4.62	2	7.3	10.3	322
Ca	2.2	2	3.17	2	5.0	7.2	560
Li	—	1	3.82	1	3.8	(5.8)	820
Na	1.8	1	3.14	1	3.1	4.9	1100
K	1.2	1	2.14	1	2.1	3.3	1750

* Parenthesis indicate that the value has been estimated.

tion. The ionization energy of the molecule may thereby have decreased with $\gamma \varphi$ and the electron will only be able to fall through $E + \delta \varphi$. γ and δ being less than one. The possibility of ionization hence occurs when $(E + \delta \varphi) + \gamma \varphi = E + (\delta + \gamma) \varphi \gtreqless J$. (When reaction between adsorbed molecules takes place the adsorption is completed. The charge of the positive zone will hence have adjusted the potential. The electron of the approaching molecule will thus not fall through the same potential difference as before adsorption occured. The ability of the surface to cause ionization is thus influenced).

The time required for an electron to cross a potential barrier decreases rapidly with the thickness of the barrier. In accordance with equation (24) the thickness of the part of the barrier due to the metal is proportional to $T^{-1/2}$. The possibility of ionization will hence increase rapidly when the temperature is increasing. *We have thus the ability of the surface to cause ionization, $E + \mu \varphi$ ($\mu < 1$), and the possibility of ionization increasing when the temperature is enlarged. The ability indicating the maximum ionization potential of a molecule that can be ionized when it comes close to the surface and the possibility of ionization being an expression only of the velocity with which the ionization, limited by the ability, will take place.* At low temperature ionization is possible when the ability is large enough, but the ionization may be so slow that it is impossible to measure it and, as long as the ionization cannot be measured, we are below the previous mentioned *minimum temperature,* a temperature that will decrease as the measuring technics is improved.

A quite similar result is arrived at if the ionization is looked upon as caused directly by the field at the surface. Also in this case it is of no use that there is a potential drop at the surface if it takes place over a relatively large zone. Only when this zone is narrowed to a certain width, set by the dimensions of the approaching molecule, ionization is possible. Considering the electron-affinity of the metallic ions at the surface, an expression of the ability to cause ionization similar to the above is also arrived at, likewise when considering ionization caused by collision of the approaching molecule with those surface-electrons which have the maximum kinetic energy E.

Ionization is thus possible when $E + \mu \varphi > J$ and the ionization will proceed more rapidly when the temperature is increased. This is in accordance with *the experimentally determined ability of several surfaces to cause ionization.* Averagely $\mu = 0.3$. Approximately the ability of the surface to cause ionization is hence

$$(23) \qquad S = 28\ a^{-2/3}\, n_l^{\,2/3} = 1.08\ E.$$

It must be borne in mind that *μ also is a function of the structure of the approaching molecule.* Discrepancies are thus caused. That

the ability is proportional to $a^{-1/3}$ is directly demonstrated by admixture of palladium to a copper catalyst whereby the lattice is increased as the proportion of carbon monoxide adsorbed on the surface from a mixture of hydrogen and carbon monoxide will increase. (As hydrogen has an energy of ionization of 15.37 volts and the monoxide 15 volts and as the ability of pure copper is about 15.9 volts a decrease in this ability will increase the proportion of monoxide adsorbed).

Considering a molecule with an energy of ionization J coming close to the metallic surface and $P \geqq J$ an electron from the molecule will make a transition to the metal, i. e. ionization occurs, and the energy

(28) $$A = P—J$$

is released. If on the other hand $J > \varphi$ an electron of the surface electrons will jump back to the formed ion which becomes neutralised. *The molecule coming close to the surface is hence ionised intermittingly. Such intermitting ionization produces adsorption.* In the chapter on adsorption (Charpter II) such ionisation is assumed and it is shown how adsorbed molecules consist of neutral and ionized molecules. If the adsorption is R and α R is the ions present ($\alpha < 1$), the energy released per molecule adsorbed is α (P—J). The positive ion formed will move to a zone, *the positive zone,* close to the surface where its potential energy is a minimum. The ion thus gains a kinetic energy, B, whereby heat is developed. The adsorption heat evolved will be

(29) $$H = \alpha \ (P—J) + B.$$

Considering molecules with electron-affin.._ ____ an energy of ionisation $J > E + \mu \ \varphi$ only negative ions are produced which will be adsorbed. If $J < E + \mu \ \varphi$ positive ions can be produced but the adsorption of negative ions may be the dominant. When negative ions are adsorbed the work function, φ, is increased. When oxygen is adsorbed on platinum the work function is thus increased to 8.5 volts. For tungsten the work function is increased to 9.2 volts. A clean tungsten surface will adsorb caesium (I. P. 4.3 volts) and

caesium ions will evaporate from such surface. On the other hand copper atoms (I. P. 7.7 volts) adsorbed on tungsten will not evaporate as ions but, as soon as the work function is increased to 9.2 volts by previous oxygen adsorption, copper ions will evaporate, whereas this will not be the case when mercury atoms (I.P. 10.4 volts) are adsorbed on a tungsten surface covered by oxygen. As the negative oxygen ions together with the surface-electrons form a negative charged cloud above the surface, the cloud and its image will produce a field between the cloud and the surface. The ability of the oxygen covered surface to cause ionization is thus not limited to the field causing the increased work function. Mercury may thus be adsorbed on the oxygen covered tungsten surface as ions but, as there is a probability that a positive ion whose ionization energy is greater than the work function can capture an electron even at some distance from the surface, no mercury ions will evaporate. The ability to cause ionization should thus for an oxygen covered surface be

(30) $$S = \Phi + P,$$

where Φ is the work function of the surface and P an inner potential.

On an oxygen covered surface of platinum, sulphur dioxide may thus be adsorbed as positive ions that will react with the negative oxygen ions. The formation of sulphur trioxide is thereby catalysed.

When positive ions are produced at the surface the ions gain kinetic energy in moving from the zone where the ionization takes place, a zone which shall be termed the »ionization zone«, into the positive zone, where the potential energy is a minimum. Such kinetic energy will be distributed amongst the ions and the molecules of the positive zone whereby the temperature of the zone is increased, i. e. heat is evolved. The electron transposed from the molecule to the metal also gain kinetic energy and in accordance to (29) the adsorption heat is $H = \alpha (P—J) + B$, where $\alpha < 1$ and B the heat developed when the ions formed move into the positive zone. If the maximum kinetic energy of the free electrons is considerably greater than the ionization energy of the molecules

brought close to the surface the ionization zone will presumably be on the outer side of the positive zone. When, in this case, the adsorption produced by the ionization is increased, the ionization zone will move closer to the surface where the possibility of ionization is larger. The distance between the ionization zone and the positive zone is thereby decreased. The kinetic energy acquired by the ions in moving into the positive zone is thereby lowered. Also the energy gained by the transposed electron is decreased, viz: *the heat of adsorption decreases by increasing adsorption.* When the adsorption increases, the charge of the positive zone is enlarged. The zone will therefore move closer to the surface. The distance between the ionization zone and the positive zone is thus increased, and it is possible that the heat of adsorption will increase after having passed a minimum. When the adsorption is further increased the heat of adsorption will again decrease as the influence of the charge of the positive zone is limited; a maximum is thereby produced. Experiments show that carbon monoxide ionized by 15 volts in the gas phase show such minimum and maximum in the heat of adsorption when adsorbed on copper, where $E + 0.3 \varphi = 15.9$ volts. When the ionization energy of the molecules is quite close to $E + 0.3\varphi$ the heat of adsorption will increase to a maximum and then decrease. Hydrogen ionized in the gas phase by 15.37 volt-electrons show such a maximum in the adsorption heat when adsorbed on copper. If $E + 0.3 \varphi$ is much larger than the ionization energy, the ions may at the outset of the adsorption be in a higher energy state than the normal. Dissociation of the ions is thus favoured. The apparent heat of adsorption may then be the difference between the true heat of adsorption and the energy of dissociation. When the adsorption is increased the relative dissociation will diminish, viz: the apparent heat of adsorption will increase until the increase is counteracted by the normal decrease in the true heat of adsorption. Hydrogen adsorbed on nickel, for which $P + 0.3\varphi = 20.1$ volts shows an adsorption heat varying in accordance herewith. The heat of adsorption for the first amount of hydrogen on nickel is 0.6 volt (about 13.500 calories), the dissociation energy of hydrogen ions

is 2.6 volts, the true heat of adsorption is thus 4.2 volts. When the temperature is increased the adsorption per unit of surface decreases, the heat of adsorption per gram molecule adsorbed will thus increase. For the same reason poisoning of a catalyst may increase the heat of adsorption when the ionization zone is outside the positive zone.

If two metals come close to each other so that the outermost part of their surface-electrons come into contact, a potential difference

$$\frac{k\,T}{e}\,\ln\,\left(\frac{n_2}{n_1}\right)^{1/3}$$

is produced (n_1 and n_2 are the number of free electrons per cc of the two metals). This difference is small. For Al-Zn the difference is 0.56×10^{-2} and for Al-Fe 0.98×10^{-2} but, when the metals come closer to each other the difference will increase rapidly. The measured contact potential between Al-Zn is 0.29 volt, Al-Fe 0.87, Fe-Ni 0.21, Li-CuO 1.3, K-Pt 2.8, Hg-Zn 0.17 and C-Cu 0.13 volt which is in quite good agreement with the mentioned succession of the metals. When molecules forming positive ions are adsorbed on the surface of a metal the density of the surface-electrons increases, the potential difference between such metal and a metal with a higher density of the surface-electrons will therefore decrease when the adsorption increases. The measured potential difference between carbon on which ammonia is adsorbed and copper is 0.079 volt. When hydrogen is adsorbed 0.096 and when nitrogen 0.13 volt, which is in agreement with the above as ammonia has a lower energy of ionization than hydrogen, the ammonia adsorption is therefore the largest and, as nitrogen cannot be ionized by carbon, the presence of nitrogen does not influence the potential difference between carbon and copper. When negative ions are adsorbed the potential difference will increase. The difference between carbon on which oxygen is adsorbed and copper is thus increased to 0.142 volt.

The decrease in energy of activation caused by the presence of a catalyst is due (1) to the decrease produced by the ionization,

which will not vary from catalyst to catalyst as long as ionization of the product most difficult to ionize is yielded, and (2) to a decrease caused by the evolution of adsorption heat, a decrease which will vary from catalyst to catalyst. We thus have the apparent energy of activation

(31) $$A_{app} = A_h - \triangle A - \lambda_A + \lambda_B,$$

where A_h is the activation energy necessary in the homogeneous reaction, $\triangle A$ the decrease due to ionization, λ_A the heat of adsorption of reactants and λ_B the heat of adsorption of the products of reaction. The decomposition of ammonia on platinum takes place with a velocity inversely proportional to the pressure of hydrogen present, which shows that ammonia as well as hydrogen are ionized. Ammonia is ionized by 11.1 volts and hydrogen by 15.37. E + 03.φ is for platinum 16.3 volts. The apparent heat of activation is on platinum less than 4.5 volts, which is the total activation required for the homogeneous changes. On tungsten the heat of activation is 1.8 volts. Considering the heats of adsorption we have for tungsten $A_h - \triangle A = 2.5$, $\triangle A$ is thus about 2 volts. As the decrease in energy of dissociation when nitrogen is ionized is 2.3 volts and for hydrogen 1.8 volts, the *ionization* of ammonia on the active surface is hence *able to account for the decrease in energy of activation*. The homogeneous decomposition of nitrous oxide require an energy of activation of 2.6 volts, on platinum the heat of activation is 1.4 volts. The ionization energy of N_2O is 12.9 volts, nitrous oxide is thus ionised by platinum. Considering the adsorption heats $\triangle A$ is about 0.4 volts. The decrease in energy of dissociation when oxygen is ionized is 0.6 volt. *Ionization* of nitrous oxide on the surface of platinum is hence *able to account for the decrease in energy of activation.*

Oliphant has shown by electron-emission that a nickel surface with four to seven layers of alkali behaves as one of pure alkali metal. Van Praagh has shown that there is a minimum thickness for a metallic film which shall be catalytically active, as a film of metal deposited by molecular rays of the metal in question showed no activity as long as it was only a few molecules thick but, as

soon as the thickness reaches 6 molecules the catalytic activity was established in the case investigated. Townes and Roller[76] demonstrated that cadmium films deposited on a glass plate cooled by liquid air in a molecular beam apparatus becomes conducting at a thickness of $2\text{-}7 \times 10^{-7}$ cm and have a critical thickness of $6\text{-}8 \times 10^{-7}$ cm, at which the resistivity is approximately fifteen times that of the bulk metal. *The catalytic activity thus sets in when conduction is established, viz. when the activity of the free electrons commences.*

Harker[82] has demonstrated that the catalytic union of ethylene and hydrogen in the presence of a copper catalyst is accelerated by X-radiation and the effect has been traced to an increased adsorption of hydrogen on the surface of the catalyst. It was showed that the radiation had no effect in bringing about the union when the metallic catalyst is not present. Further the radiation had no effect in increasing the adsorption on the diatomaceous earth used as support for the catalyst. As the radiation is able to displace electrons from atoms and as radiation may increase the kinetic energy of the electrons of the metal, the increase in the catalytic power when the catalyst is irradiated can be due to (1) an increase in number or in energy of those surface-electrons having a high kinetic energy or (2) an increase in the possibility of the presence of lower empty levels. In both cases *the ability of the metallic catalysts to cause ionisation is enlarged by irradiation and thereby the adsorption and the catalytic effect.*

Taylor suggested that so-called peak areas were associated with special activity. Steacie and Elkin[77] demonstrated, however, that the rate of decomposition of gaseous methyl alcohol over solid and liquid zinc was directly dependent on the temperature, there being no discontinuity at the melting point. It was therefore concluded that the entire surface is uniformly active. A progressive removal of the postulated peak areas by poisoning caused, furthermore, no change in the activation energy of the decomposition of hydrogen peroxide on platinum. It seems thus that the catalytic activity is not bound to certain areas of the surface of a single metal. The ionic

adsorption described does not involve any assumption regarding peak areas. A heterogeneous catalyst will, however, have crystal surfaces with different activity.

With regard to *the oxides,* which consists of a metallic lattice and an interpenetrating oxygen lattice, the metallic lattice is one of positive ions and the oxygen lattice one of negative. Now the metallic lattice can produce »free« electrons just as in the metals. The lowest level an electron can fall to, will, however, not be that determinated by the metallic lattice and an electron coming from the exterior will not be able to fall alone to the lowest level determined by the metallic lattice but to one so much lower than this as the electron-affinity of oxygen determines; the level O—O of the diagram. The ability to cause ionisation will be proportional to P_0 of the diagram whereas the work of emergence should to a certain extend be determined by the maximum kinetic energy of the »free« electrons of the metallic lattice.[2]

In quantum mechanics there is not much difference between a metal and an insulator. In a metal the electrons are moving in all directions and, when an electric field is applied, some of the electrons will move in the direction of the field. Such electrons having jumped to a higher energy level. In insulators there are no allowed levels to which electrons can jump. A field of normal intensity is thus unable to produce an electric current through the insulator. This does not exclude that the conditions at the surface of an insulator may be similar to that at the surface of a metal. *The surface of an insulator may hence have ability to cause ionization, viz. be catalytic active.* We have thus, besides the metals, a variety of catalytic active products.

Vanadium pentoxide is thus a very active catalyst, for instance, and vanadium catalysts of the zeolite type are as good as platinum for the acceleration of several reactions.

The surface of *semi-conductors* is hence also catalytic active. The resistance of semi-conductors decreases as the number of conduction electrons increases at higher temperatures. The catalytic

activity of the surface of a semi-conductor will hence increase when the temperature is enlarged.

Even the surfaces of products like the crystals of phthalocyanine and copper phthalocyanine are catalytic active as they are able to activate hydrogen as shown by Calvin, Cockbain, Eley and Polanyi.[78]

Catalytic activity is also produced when certain molecules are agglomerated by adsorption on inactive surfaces. Bredig and Gerstner[79] were thus able to demonstrate that certain molecules anchored to organic fibres were catalytic active. This may be a clue to the understanding of enzymic action, Nyrop[3] suggested that a specific grouping of molecules containing benzene rings, double bonds, COOH groups, etc. may give raise to »free« electrons when the benzene rings, double bonds, etc. are co-ordinated. Nyrop showed how the Twitchell agent may act and pointed out that the fact »that some haematine seems to be able to produce oxidation processes is in accordance with the above mentioned suggestion as haematine contains benzene rings linked together with highly unsaturated bonds, whereby electron activity may be caused.« This activity should be the cause of the enzymic action, and the adsorption of the active molecules on a support such as organic fibres, colloids, etc. should produce the required co-ordination. That it is now shown that the surface of phthalocyanine is catalytic active is of interest in this connection, as it is related to haemin.

It may in this connection be of interest to mention that McBain and Foster[80] have demonstrated that the specific surface conductivity of close packed films of adsorbed stearic, palmitic or oleic acid is too high to be attributable solely to the mobile ions of the outher part of the adsorbed layer, and that Baumbach and Wagner[81] showed that the conductivity of nickel oxide at higher temperatures varies with the oxygen pressure in the surrounding gas and that the conduction is nearly all electronic.

When ionic adsorption of a gas takes place, the positive ions formed neutralize part of the effect of the surface electrons whereby the distance between the outermost part of the surface electrons and the surface increases, viz. the average field close to the surface

is weakened, although the potential difference between any point of the metal and points at some distance from the surface may remain constant. At a certain adsorption the field may thus be weakened to such degree that the surface is no more able to ionize the molecules. *The ionic adsorption is* hence *limited, and molecules with ionization potentials lower than that of the adsorbed gas will, when admixed, act as poison.* Bredig[43] showed that in the decomposition of hydrogen peroxide on platinum, hydrogen sulfide destroyed the activity to a much larger degree than hydrogen cyanide. The ionization potential of hydrogen Sulphide is 10.4 and of the cyanide 14.8 volts. Besides the limit of the adsorption set by the weakening of the field, impinging molecules and the presence of the surface-electrons counteract the adsorption; the adsorption may thus never reach the limit set by the field. *At high temperatures the field is strengthened so much that the influence of the adsorbed positive ions is decreased. Poisons are thus more active at low than at high temperatures;* this is a well-established fact. A given reaction may also be self-poisoning. The temperature will therefore have to be above a certain value before the reaction takes place with a considerable velocity. Now the catalysts with high ionizing power are more exposed to poisoning than those with lower. In hydrogenation processes, for instance, platinum and palladium are thus active at room temperature, whereas the more active iron and nickel require a higher temperature. That argon is not as strongly adsorbed as nitrogen although their ionization potentials are of the same order is due to a difference in requirement to the distance over which the potential drop at the surface shall take place, argon demanding a smaller distance than nitrogen. (Argon has, for instance, a smaller sectional area than the nitrogen molecule).

CHAPTER VIII.

THE CATALYTIC EFFECT OF SURFACES.

The activity of surfaces as described in the previous Chapters suggests that the following laws govern the catalytic reactions produced by surfaces:

(1) In a chemical reaction furthered considerably by the presence of a surface, the surface is at the temperatures in question able to ionize those molecules among the reactants most difficult to ionize.

(2) The ability of the surface of a catalyst to cause ionization is proportional to the negative energy of the lowest empty level of the catalyst with regard to an electron outside the catalyst. For the metals this ability is approximately proportional to the maximum kinetic energy of their »free« electrons.

(3) The field strength at a metallic surface increases when the temperature is enlarged. If ionization shall take place with a considerable velocity a certain field strength is required and thus a certain high temperature.

(4) Molecules (atoms) brought close to a surface able to ionize them are adsorbed strongly and the ionization is intermittent. When the molecules adsorbed are substituted by other having a lower ionisation potential or the ability of the surface to cause ionisation is increased, the adsorption will increase.

(5) Reaction among the intermittently ionized and thus adsorbed molecules (atoms) is a reaction between the ions of the molecules most difficult to ionize and the molecules with the lower ionization potential being in their neutral state.

(6) The apparent energy of activation of a reaction is lowered by the ionization produced by the catalyst and by a difference in adsorption heat of the reacting molecules and the resulting compounds.

(7) The velocity of reaction is increased by the lowered energy of activation and also enlarged by the increased concentration of reacting molecules at the surface.

(8) Molecules (atoms) formed during the reaction between those adsorbed depends on the ratio of the various adsorbed molecules to each other, and on the ionization potential and the molecular weight of the new molecules, as those with the highest energy of ionization and/or in certain cases the lowest molecular weight will be preferably ejected from the surface. Off boundaries on a surface between patches with different activity the ratio of molecules (atoms) to each other is different from that off the patches and, as various compounds can be produced on either side of a boundary, the ejected products will depend on the structure of the catalyst.

(9) Raised temperature, placing increased translatory kinetic energy and vibrational energy at the disposal of activation, increases the number of collisions among the adsorbed molecules (atoms) able to cause chemical reaction or dissociation besides increasing the field strength at the surface but the increment diminishes the flow through the active zone close to the surface. Raised pressure increases the flow through the active zone. When the flow is diminished by increased temperature the pressure must thus be raised to secure a certain velocity af reaction. Besides, raised pressure allows for a high space velocity. As the action caused by the saturation pressure and the varied adsorption must be taken into account, many processes are alterede by an increase in pressure.

(10) The catalytic effect is proportional to the accessible area of the catalyst.

The catalysts that are able to further a given reaction to a considerable extend are fairly restricted in properties. The investigator, who wants to determine a catalyst for the reaction ought therefore first to determine the ionization potential of the reacting molecules. He will then know the order of magnitude of the ability to cause ionization of the catalyst to be chosen as this shall be larger than the ionization potential of those of the reacting molecules most difficult to ionize. If the reaction is A + nB (n > 1), and A has the highest ionization potential, a catalyst with an ability close to this ionization potential shall be selected. If B has the highest potential the ability of the catalyst shall be taken as high as possible. When, thereby, the catalyst has been found its surface will have to be increased as much as possible by a suitable manner of preparation and a suitable support (carrier). The surface will furthermore have to be protected against sintering by the incorporation of a promoter. Thereafter the temperature and pressure is determined with due heed to the development of the right field strength at the surface, the equilibrium conditions, and the risk of self-poisoning of the surface by the reacting products. In the case of technical processes the presence of poisons will affect the choise of the catalyst. Catalysts requiring a rather high temperature to develop the field strength necessary at the surface to produce ionization will in this case be preferred to the catalysts active at lower temperatures being most exposed to poisoning. For this reasons oxide catalysts may often be preferred to metals.

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Abreviated Title.	Journal.
Accad. Lincei.	Atti della reale accademia nazionale dei Lincei.
Ang. Chem.	Zeitschriff für angewandte Chemie.
Ann. Chim. Phys.	Annales de chimie et de physique.
Biochem. Z.	Biochemische Zeitschrift.
B. P.	British Patent.
Chem. and Ind.	Chemistry and Industry.
Chem. Zentr.	Chemisches Zentralblatt.
Compt. Rend.	Comptes rendus hepdomadaires des sèances de l'acadèmie des Sciences, de l'institute de France.
J. Appl. Chem. Russia.	Journal of Applied Chemistry, Russia.
J. A. C. S.	Journal of the American Chemical Society.
J. Chem. Ind. Russia.	Journal of Chemical Industry, Russia.
J. Chem. Phys.	Journal af Chemical Physics.
J. Chem. Soc.	Journal of the Chemical Society.
J. Phys. Chem.	Journal of Physical Chemistry.
J. Phys. Rad.	Journal de physique et le radium.
J. S. C. I.	Journal of the Society of Chemical Industry.
J. State Med.	Journal of State Medicine.
Kem. Mbl.	Kemisk Maanedsblad (Copenhagen).
Nature.	Nature (London).
Naturwiss.	Die Naturwissenschaften.
Phil. Mag.	Philosophical Magasine.
Phys. Rev.	Physical Review.
Proc. Nat. Accad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Roy. Soc.	Proceeding of the Royal Society.
T. Farad. Soc.	Transactions of the Faraday Society.
Z. Electrochem.	Zeitschrift für Electrochemie.
Z. Physik.	Zeitschrift für Physik.
Z. Phys. Chem.	Zeitschrift für physikalische Chemie.